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Detection of Carbon Dioxide with Chemical Tapes

FINAL REPORT

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
MANNED SPACECRAFT CENTER
Houston, Texas

Submitted by

MELPAR, INC.
7700 Arlington Boulevard
Falls Church, Virginia

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1. INTRODUCTION

This is the final report submitted to the NASA, Manned Spacecraft Center, Crew System Division, Houston, Texas, in fulfillment of Contract No. NAS-9-2883 (Melpar Job No. 4274.00100). This report covers Melpar's efforts in developing CO_2 sensitive tapes which are capable of reacting to various levels of CO_2 after storage for long periods of time under various conditions of temperature, humidity, and pressure.

A number of improvements have been made in the packaging and in the materials used in the reaction process itself during the contractual period. Further possibilities for improvement have been found, which are discussed.

The tapes, as presently prepared, are fully capable of extended storage under various conditions. The deliverable tapes have been exposed to a large variety of conditions. Statistical analyses have been performed and are reported. In addition, the many manufacturing variables which have affected the performance of the tapes have been investigated. These are discussed in section 3.

During the course of the investigation, a study was made concerning the reproducibility of the reaction occurring between the tapes and CO_2 to define precisely the reliability that could be expected from such a device. These studies have included examination and determination of the human error associated with optically detecting the color change on these tapes.

Since the evolution of hydrazine into the spacecraft atmosphere could present a hazard to the crew, the amount of hydrazine which would be expected to evolve from the tapes was determined and the effects evaluated. The response time of the tapes in a 4000-foot/minute flow of nitrogen at 5 psia was also determined.

2. DESCRIPTION OF THE THE CO_2 DETECTORS

The carbon dioxide detectors as they appear in their final form are shown in figures 1 and 2. Figure 1 shows the detector before it is opened for exposure to CO_2, while figure 2 shows the opened detector.

The badge itself is made of aluminized Mylar-polyethylene laminate with a polyethylene lining. The laminate (3-mm Scotch-Pack pouch) is polyethylene-Mylar-vapor deposited aluminum-polyethylene (heat sealable on both sides). Looking at the detector in figure 1 and imagining that one can see depth-wise through the detector, the layers of material are the laminate lined with 4-mil polethylene (forms the two cover flaps), 4-mil polyethylene (sealed to make pockets for the reference tapes), the laminate, 4-mil polyethylene, pockets for the sensitized tapes, 4-mil polyethylene, and the laminate. All layers of material, except the two that form the tear tabs (cover flaps), are sealed together in a manner that forms four pockets, one for each of the four sensitized tapes.

The ends of the tear tabs and the back flap are corrugated to permit one to grip the ends better when opening one of the detectors. The detector (number 4140) can be seen on the left tear tab and the inspector's stamp appears on the right tear tab. The black numbers (2, 4, 6, and 8) above the pockets designate the levels of sensitivity of the tapes in each of the four pockets. All seals, except for the seal that runs lengthwise across the detector below the numbers 2, 4, 6, and 8, and above the reference strips, are made before the sensitized tapes are placed in the detector.

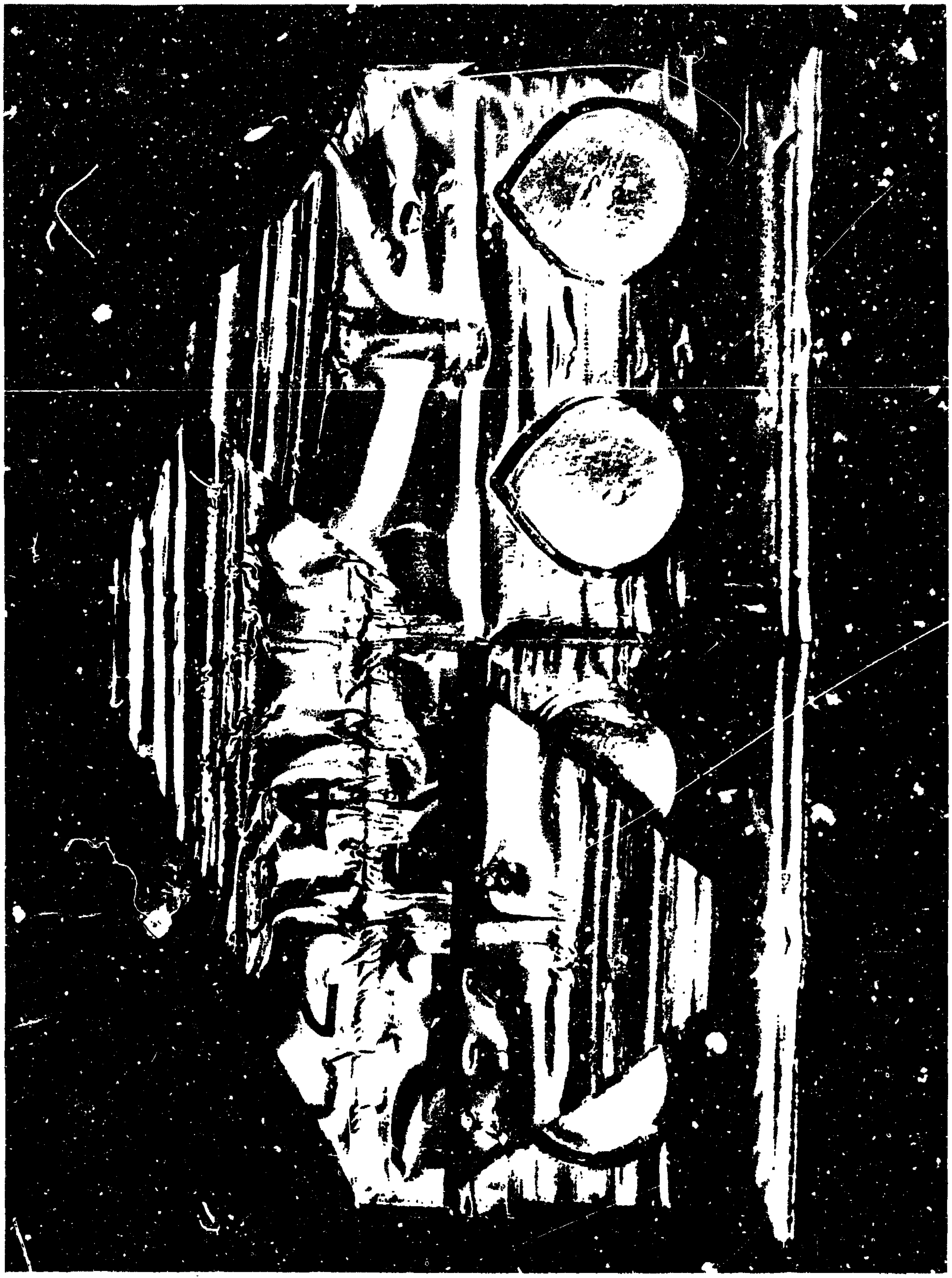


Figure 1. Photograph of Completed (Closed) Detector

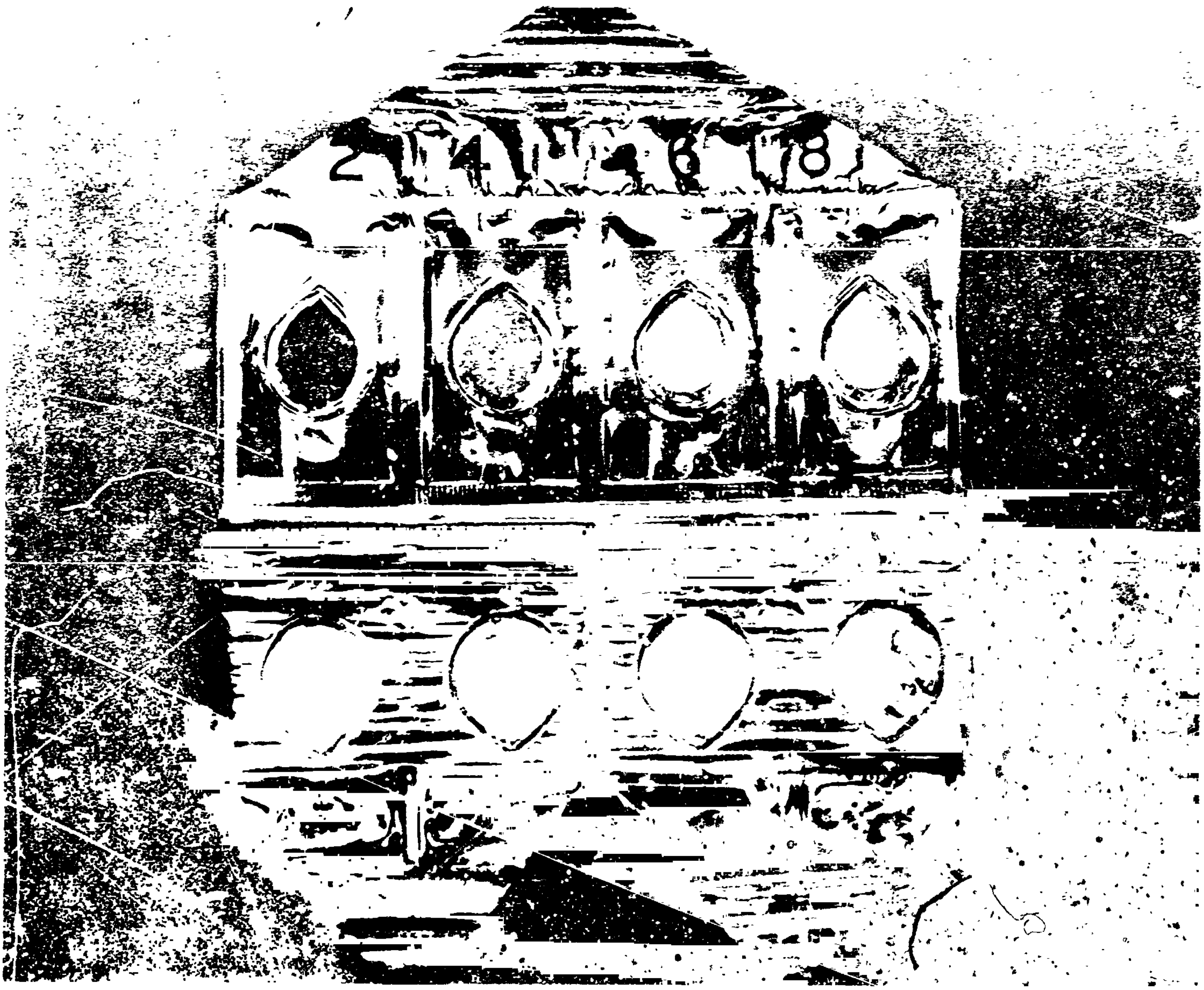


Figure 2. Photograph of Opened Detector

The exposed sensitized tapes which can be seen through the tear drop ports of the opened detector (figure 2) are inserted into the badge from behind the large back flap. The seal between the numbers and the reference strips is made after the four colorless, unexposed sensitized tapes are inserted into the badge.

The reference strips which can be seen around the 2- and 4-mm ports are blue-violet (Crystal Violet) in color, and the 6- and 8-mm reference strips are a dark pink (Basic Fuchsin). To be able to distinguish one exposed tape from another, one corner of both the 4-mm tape (blue-violet when exposed) and the 8-mm tape (pink when exposed) is notched. The 2-mm tape (blue-violet when exposed) and the 6-mm tape (pink when exposed) do not have any notches.

Table 1 gives the dimensions of the CO_2 detectors and their components.

TABLE 1

DIMENSIONS OF CO_2 DETECTORS

Part	Size
Completed detector (including tear tabs)	2-3/4 inches wide, 4 inches long, 1/8 inch thick
Numbers 2, 4, 6, and 8	1/4 inch high
Reference strips	1-1/8 inches long, 3/4 inch wide
Sensitized tapes	1 inch long, 5/8 inch wide
Tear drop ports	1/2 inch high, 7/16 inch across

3. SUMMARY OF SPECIFICATIONS FOR CARBON DIOXIDE DETECTORS

The CO_2 detectors delivered to NASA, Manned Spacecraft Center, Houston Texas, had to meet certain requirements as determined by NASA and Melpar. The list of specifications given below is the most recent and, therefore, includes the requirements in their corrected forms only and not as they appeared in the original contract. The original contract has been modified several times as the work progressed.

Each of the badges in the four most recent shipments of detectors had to meet the following requirements:

a. Each detector was to be capable of detecting the presence of carbon dioxide at each of the following partial pressure levels: 2, 4, 6, and 8 millimeters of mercury.

b. Concentration within 10% of a given partial pressure of carbon dioxide was to be indicated by a distinct color change in one section of the detector which was clearly designated as associated with that particular carbon dioxide partial pressure.

c. A quality program was to be established and maintained for the packaging material to ensure that a consistent quality was obtained. The packaging was to have prevented deterioration and/or aging of the chemical tapes in the detector by any photochemical, oxidative, or other degenerative process.

d. The detectors were to be capable of detecting carbon dioxide as specified in a above, under the following conditions:

(1) Temperature: 40° to $120^{\circ}F$.

(2) Pressure: 23.5 to 3 psia.

(3) Relative humidity: 15% to 100%.

e. Specific features and dimensions of the detectors were to be as follows:

(1) Size including tear tab: 2-3/4 inches wide, 4 inches long, 1/8 inch thick.

(2) Tear tab: Approximately the same length and width as the badge. The ends of the tear tab were to be rough so that they could be easily handled.

(3) Reference strips: Encircling each detecting strip hole.

(4) Detecting strip hole size: 1/2 inch diameter.

(5) Detecting strip color: Blue to indicate 2 and 4 mm of CO_2; red to indicate 6 and 8 mm of CO_2.

(6) Response time: 35 seconds, ± 6 seconds.

f. The packaged detectors were to be capable of being stored without deterioration for a period of not less than 3 months under the following conditions:

(1) Temperature: 20° to 90°F.

(2) Pressure: 14.7 psia.

(3) Relative humidity: 15% to 100%.

g. Qualification test requirements: The contractor was to perform the environmental tests included in table 2 on the carbon dioxide detection tapes. Each detector was to meet all requirements of response after exposure to these environments.

TABLE 2

QUALIFICATION TEST REQUIREMENTS

Test	Temp	Pressure	Gas	Humidity	Time
High-temperature oxygen	120°F	5.5 psia	100% O_2	~50%	48 hours
Decompression	120°F	1.47×10^{-5} psia	Air	~50%	24 hours
Low temperature	0°F	1 atm	Air	--	4 hours
Pressure	~75°F	23.5 psia	Air	~50%	1 hour
Temperature-pressure	0° to 120°F	1.47×10^{-5} psia	Air	--	24 hours
Humidity	68° to 120°F	1 atm	Air	95%	240 hours (cycled every 24 hours)

4. SELECTION OF REACTION, REAGENTS, AND MATERIALS FOR CO_2 SENSITIVE TAPE PREPARATION

The major problem of this work has not been the production of a chemical tape which will detect carbon dioxide, but instead the production of a tape which can be stored under various conditions and still respond to a given partial pressure of CO_2. There are a number of color reactions which can be considered in connection with a carbon dioxide detector. These reactions fall into two categories: (1) a pH indicator and (2) a triphenylmethane dye decolorized with a reducing base. Each of these will be discussed separately in the following paragraphs. The different materials for manufacturing the sensitive tapes were also carefully selected. For each, a number of tests were made to select the most suitable. For packaging, a plastic laminate was selected which permits the longest storage time.

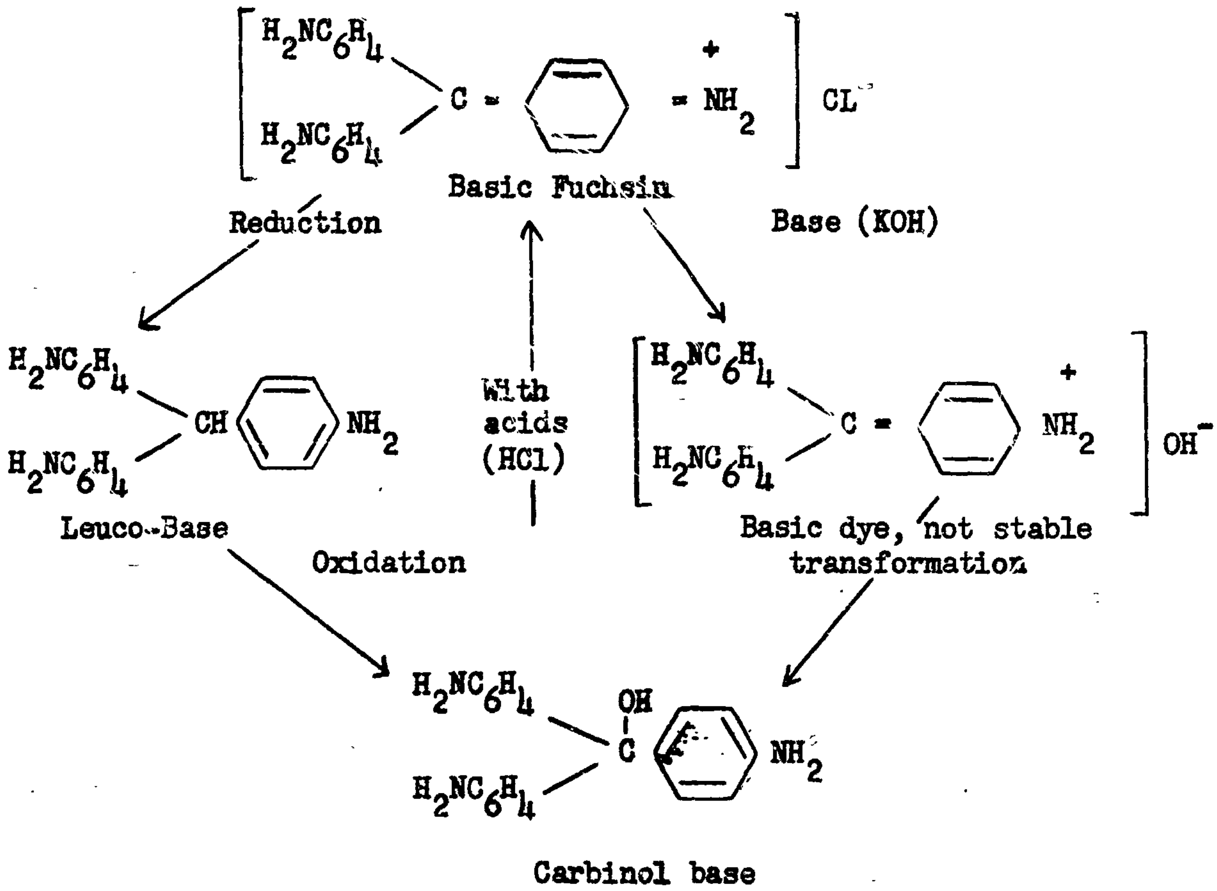
4.1 Selection of Reagents

Now many colored reactions for carbon dioxide are known. Some of the known color reactions are those associated with the color change of a pH indicator. This type of color reaction is not specific since any acidic gas (H_2S, SO_2, or NO_2) will lead to a color change of the indicator. A more specific reaction is carbonate precipitation with the alkali earth metals. However, it is difficult to see such precipitates on a reactive paper, and the intensity of the precipitate cannot be observed.

Another method of detecting carbon dioxide through a color reaction is to use triphenylmethane dyes decolorized with hydrazine. Such a reagent system will change from colorless to a distinct color when exposed to CO_2, and the intensity of the color will be proportional to the CO_2 concentration.

Indicators for acid-base reactions change color with the pH of the solution. Carbon dioxide is acidic and will change the color of an indicator from the basic color to the acidic color. Phenolphthalein is pink in a basic solution and colorless in an acidic solution. This is a commonly used indicator for titrimetric CO_2 determinations. As a detector it is not considered suitable, because it changes from pink to colorless. Thymol Blue and Thymolphthalein are also indicators which will change color with the addition of CO_2; however, both are blue in the basic solution and fade to yellow or colorless when acidic. A good indicator for CO_2 detection is Nile Blue. The basic solution of this indicator is pink; when the pH is lowered by carbon dioxide, the color changes to blue. Very good tapes were prepared with this indicator. The disadvantage of these tapes was the lack of stability. The basic solution of the indicator oxidized very rapidly, and the indicator was destroyed in 8 days.

The triphenylmethane derivatives with a normal benzoidal structure are transformed to a Leuco-Base with reducing materials. The triphenylmethane dyes are generally imonium salts. With alkalies they are transformed to the carbinol bases. These transformations of Basic Fuchsin are as follows:



CO_2 acting as an acid redevelops the original color of the dye present in the leuco-form.

The following dyes were tested experimentally: Malachite Green, Methyl Violet, Basic Fuchsin, Victoria Blue, Crystal Violet, Aniline Blue, and Pararosaniline. The best results for CO_2 reagent were obtained with Crystal Violet and Basic Fuchsin. Both decolorize easily, Crystal Violet with less hydrazine than the Basic Fuchsin, and the original color is restored by gaseous carbon dioxide. This was not the case in some of the other triphenylmethane dyes mentioned above.

4.2 Selection of Solvents

The solvent for the reagent should preferably be an alcohol, because the reaction is carried out more easily and more rapidly to completion in this solvent. There are many properties of a given alcohol which must be taken into consideration before it may be used as a solvent for the reagents. For instance, the alcohol must be a good solvent for the triphenylmethane dye and also be miscible with hydrazine. Methanol, ethanol, ethylene glycol, and diethylene glycol were the solvents tried for this purpose.

Methanol is a good solvent for the dyes and is miscible in all proportions with hydrazine. Tapes soaked in a reagent solution made with methanol were very uniform and responded well when freshly prepared. However, after 24 hours of storage in a Scotch-Pack pouch, they had completely deteriorated. No response or color formation was observed when it was exposed to an atmosphere containing CO_2.

Ethanol is also a good solvent for most of the triphenylmethane dyes. The reagent made with ethanol is easily absorbed by the filter paper. The tapes made with an ethanol solution, when stored in sealed pouches, accumulated the dye on the edges and, after several days of storage, the color development was nonuniform. The boiling point of ethanol is obviously too low to give stable tapes.

Ethylene glycol was finally selected as the best solvent. It dissolves the dye slowly, but, with a little heating, the dissolution can be accelerated. It is miscible with hydrazine and has a high boiling point which assures that it remains on the filter paper and thereby retains the reactivity of the tape.

Diethylene glycol is as good a solvent as ethylene glycol. There is no advantage to its use, however, because its viscosity is higher than that of ethylene glycol. Thus, it soaks into the filter paper more slowly.

4.3 Selection of Support

As support for the reagent solution, filter paper seemed to be the most likely choice. Various grades of filter paper were tested in an attempt to find the most suitable paper for absorption of the reagent solution as well as for handling and storage. Glass filter paper, because of its inertness, was the first to be tried. This paper was very difficult to handle and it gave spotted tapes due to the irregularity of the surface of the paper.

Whatman's spot test paper, which was successfully used in NO_2 detector tapes, proved to be too thick and porous. Whatman's No. 5 paper gave tapes that were neither uniform nor reproducible. These difficulties could have been due to the fact that this paper was not as quantitatively pure as are some other grades. Quantitative and hard filter paper (Whatman No. 54) was also tried and was found to be too brittle when wet. Whatman No. 41H (or 541) has been used with the most success. It is rather hard, yet highly absorbent. This paper was the final selection, and all tapes were prepared with it.

4.4 Packaging of Tapes

The packaging of the four sensitized tapes (2, 4, 6, and 8 mm) is also very important. The tapes must be separated from each other to maintain their own sensitivity level. Each one contains hydrazine and, without tape isolation, it would equilibrate around the different tapes. This equilibration would lead to an equalization of all tapes, and they would respond only to one level of CO_2 concentration.

The quality of the packaging material also is important. A number of different plastic materials were examined for their permeability to air or oxygen over a period of hours. Oxygen will degrade the chemical reagents. Those having low values of oxygen permeability were selected for the containers of the CO_2 tapes. These were Mylar, Tedlar, Teflon, aluminized Mylar, aluminized Mylar with polyethylene, polyethylene, aluminum foil with polyethylene, and Aclar.

Mylar alone, which has a very low permeability to oxygen, cannot be used because it is not heat sealable. Tedlar was used for early deliveries under the contract. It is very resistant to the attack of the chemicals in the tape; however, it is difficult to make a tear-open seal with it. Teflon is not heat sealable and cannot be used. Aluminized Mylar offers very good protection against air leaks. It is, however, heat sealable only on one side and because of this some arrangements were made to permit sealing the tear-open hole. However, the chemicals in the reagent penetrate the polyethylene layer and etch the Mylar layer underneath. This etching made it necessary to line the inside of the pocket with a second film of 4-mil polyethylene. This was the final material which was used for the fabrication of the CO_2 detector badges.

Nevertheless, the material used had failures because the Scotch-Pack or aluminized Mylar, which is a laminate, delaminates (the layers separate). This delamination causes premature oxidation of the sensitized tapes and failures occurred. In section 11.2 some of the materials for badge preparation are described and discussed for possible future use.

5. VARIABLES INVESTIGATED IN THE PREPARATION OF TAPES

5.1 Concentration of Reagents

The detection of CO_2 at various concentration levels is dependent on a chemical reaction between the gas and the basic form of a chemical dye. A reaction such as this is quite dependent on the concentration of the reagents, and thus optimum reagent concentrations must be determined and rigidly controlled. Initially, dye concentrations between 0.02% and 0.2% were tested. The higher concentration was found to be more effective because a darker color resulted during the 30-second exposure, yielding more reliable results.

Since the variations in the concentration of hydrazine controls the reaction rate at which the tapes respond to the various CO_2 levels, it was necessary to ascertain the minimum levels of hydrazine necessary to convert the dye to its basic form and to permit proper color changes when the dye was exposed to CO_2. In the case of Crystal Violet, the concentration of hydrazine required to convert the 0.2% dye is 6.28%; while for 0.1% Crystal Violet, 3.2% hydrazine concentration is required. Initially, good results were obtained with 0.1% Crystal Violet dye, and concentrations of hydrazine at the 5%, 10%, 15%, and 20% levels gave tapes sensitive to 2-, 4-, 6-, and 8-mm levels of CO_2. In all cases, ethylene glycol was used as the solvent.

Table 3 lists the concentration levels used for Crystal Violet and Basic Fuchsin reference tapes which were examined during the early work discussed here. The basic problem with the development of a device such as the chemical reaction tapes is to find the delicate balance between the amount of dye used and the amount of decolorizing agent required to change the dye into its basic state. If insufficient dye is used in the preparation

TABLE 3

CONCENTRATION LEVELS FOR CRYSTAL VIOLET AND BASIC FUCHSIN REFERENCE TAPES

Crystal Violet Reference Tapes:

References	Concentration of Crystal Violet Used
1:4 of 0.1% dye	20.0×10^{-3}%
1:10 of 0.1% dye	9.1×10^{-3}%
1:20 of 0.1% dye	4.8×10^{-3}%

Basic Fuchsin Reference Tapes:

Reference	Concentration of Basic Fuchsin Used
1:8 of 0.5% dye	5.6×10^{-2}%
1:16 of 0.5% dye	2.9×10^{-2}%
1:32 of 0.5% dye	1.5×10^{-2}%

of the tapes, the color change will be too slight for certain detection. If too much dye is used, the final color will be quite uneven. It is necessary to control the hydrazine concentration closely, since it is this reagent that controls the effective sensitivity of the tapes. This is clearly shown in table 4.

As shown in the fifth monthly report, a study was made which illustrates the degree of control of the hydrazine which must be maintained to ensure the production of tapes that will meet the requirements. Crystal Violet (0.1%) tapes were reacted with hydrazine concentrations of 6.5%, 8.5%, 10.5%, 12.5%, 14.5%, and 16.5%, and then tested with 2- and 4-mm CO_2 atmospheres.

The tests were also made with 0.2% Basic Fuchsin tapes (at 6- and 8-mm partial pressures of CO_2) using hydrazine concentrations of 4.5%, 5.5%, 6.5%, 7.5%, 8.5%, and 9.5%.

The results of the above tests are shown in figures 3 and 4. It is readily seen that the response time in each case is a linear function of the hydrazine concentration. Since the hydrazine concentration is a critical factor in the fabrication of the reactive tapes, the commercial hydrazine was analyzed to determine the exact hydrazine content. The solutions made for the preparation process were then made on the basis of the exact hydrazine content as determined in the laboratory.

5.2 Soaking Time of Filter Paper in the Reagents

To determine the most reproducible method for tape preparation, an investigation was made to determine the optimum conditions for adding the dye to the absorbent paper. A gravimetric procedure, i.e., determing the weight of dye absorbed, was found to be the best way to study the process.

TABLE 4

HYDRAZINE CONCENTRATIONS

	CO_2 Levels	Hydrazine Conc. (%) for Tapes Having 30 Sec. Response Time	Hydrazine Conc. (%) for Tapes Having 60 Sec. Response Time
Crystal Violet Tapes	2 mm	7.58	9.38
	4 mm	9.38	11.48
	6 mm	11.48	13.98
	8 mm	13.98	16.48
Basic Fuschin Tapes	6 mm	4.15	6.65
	8 mm	5.38	8.00

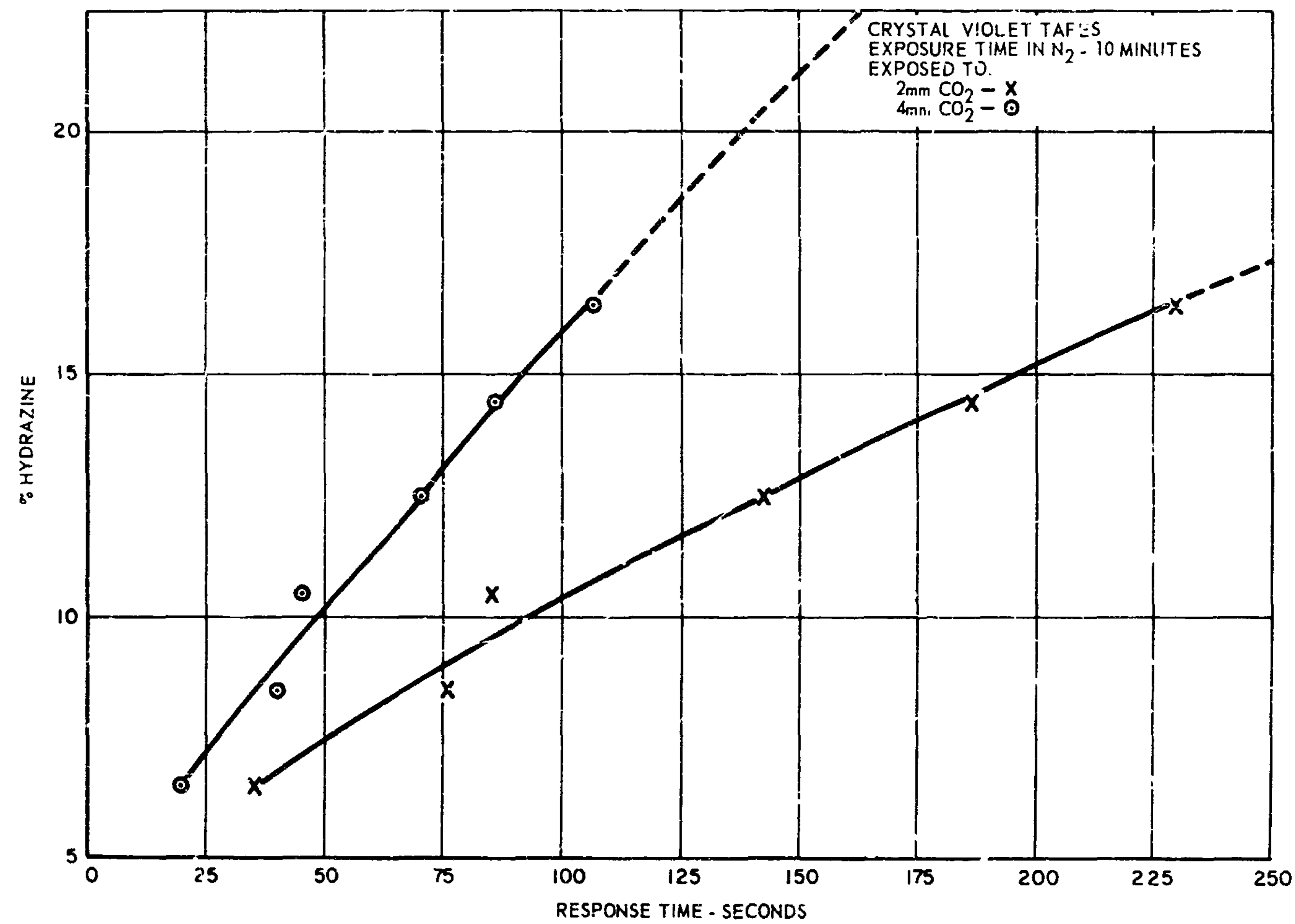


Figure 3. Hydrazine Concentration of Crystal Violet Tapes Versus Response Time

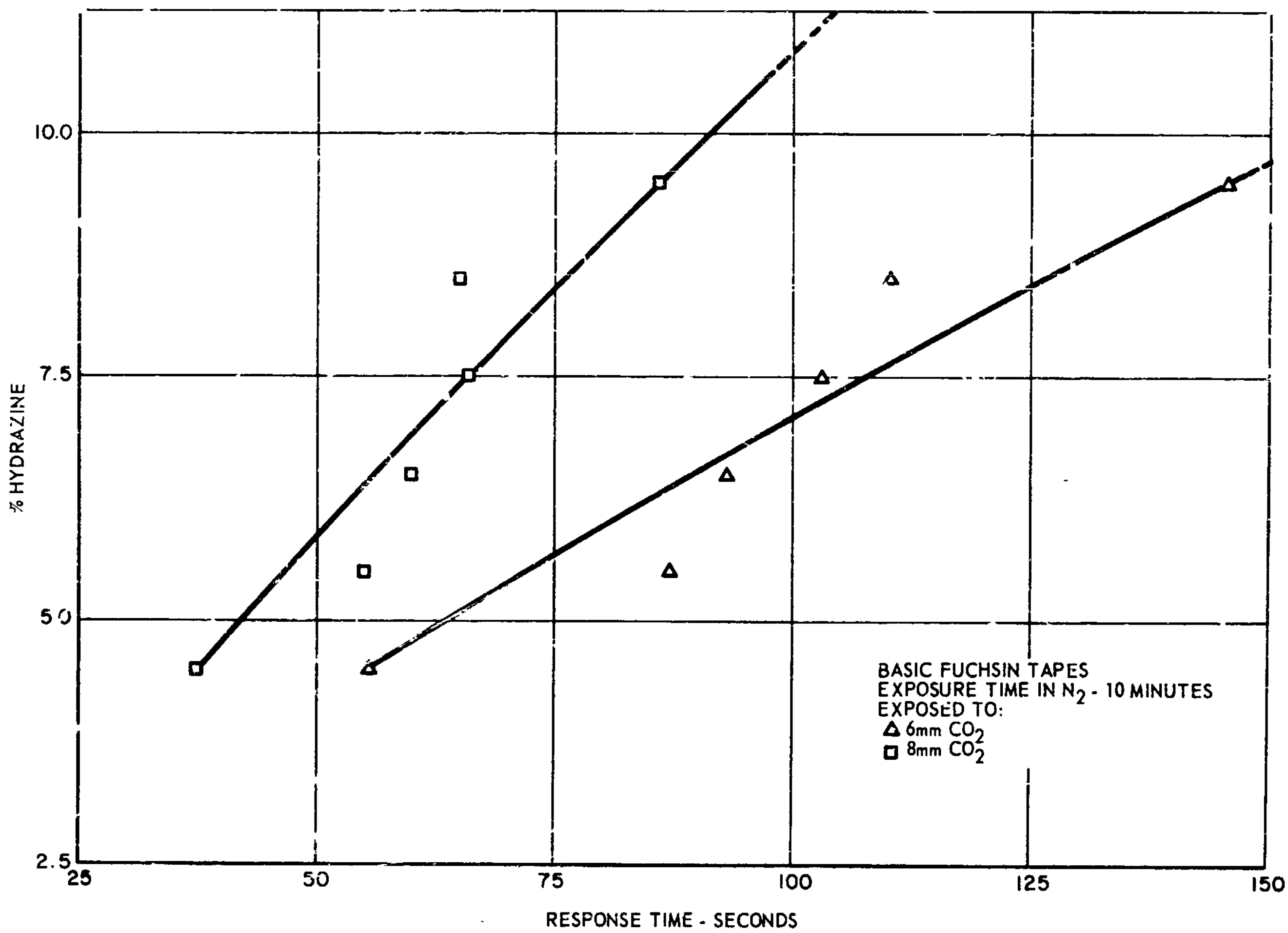


Figure 4. Hydrazine Concentration of Basic Fuchsin Tapes Versus Response Time

A number of tapes were immersed in the dye solutions for periods of time ranging from 1 to 60 minutes, and their response times to a 4-mm CO_2 atmosphere were evaluated. The results, as shown in figure 5, indicate a sharp increase in response time during the first 15 minutes, after which the curve tends to level off. To keep the response time within the allowable limits, however, it is obvious that approximately a 1-minute soaking time is the maximum that can be used.

5.3 Blotting Procedures

To study the effects of various methods of blotting the tapes, several different procedures were tried. In each procedure, six tapes were weighed, both before and after being soaked in reagent solution, to determine the amount of solution taken up by each tape. The six tapes treated with reagents by each of the methods were cut in half and tested for response times.

The tapes were made from the same filter paper (Whatman No. 41H or No. 541) and the same reagent solution (12.50% hydrazine and 0.1% Crystal Violet in ethylene glycol). This was the 4-mm tape. All tapes were soaked in the reagent solution for 1 minute each, drained for about 5 seconds, and then placed on a blotting towel. The tapes were tested in pockets with a 4-mm partial pressure of CO_2 to a 1:10 Crystal Violet reference level. The results of these tests are given in tables 5 through 13.

5.3.1 Preparation Procedure A

In Procedure A, the six tapes to be used for determining the weight of reagent uptake were soaked individually and then placed on a paper towel in order (No. 1 to No. 6). The tapes were left on this "wet" paper towel from 6 minutes to 1 minute in the given order before they were blotted, and

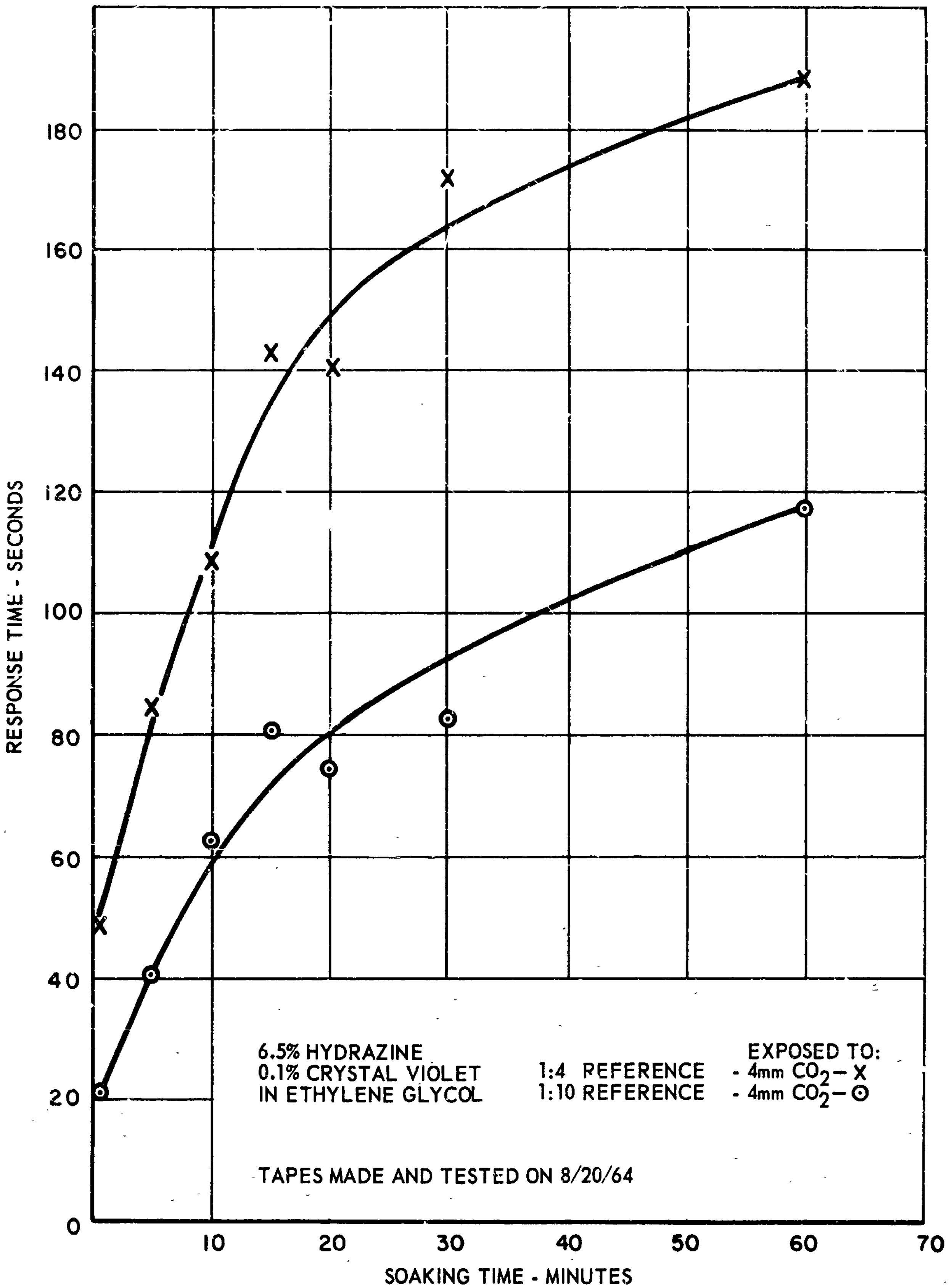


Figure 5. Effect of Soaking Time on Response Time

TABLE 5

RESULTS OF TAPES PREPARED BY PROCEDURE A

Tape No.	Weight of Tape (g)	Weight of Solution on Tape (g)	Percentage Uptake of Solution	Tape No.	Response in Seconds: # Half of Tape	Response in Seconds: # A Half of Tape
1	0.1028	0.0676	65.76	1	95	91
2	0.1047	0.0636	60.74	2	72	62
3	0.1036	0.0625	60.33	3	86	79
4	0.1025	0.0670	65.37	4	73	64
5	0.1049	0.0610	58.15	5	67	60
6	0.1029	0.0581	56.46	6	59	53

TABLE 6

RESULTS OF TAPES PREPARED BY PROCEDURE B

Tape No.	Weight of Tape (g)	Weight of Solution on Tape (g)	Percentage Uptake of Solution	Tape No.	Response in Seconds: # Half of Tape	Response in Seconds: #A Half of Tape
1	0.0823	0.0317	38.52	1	146	102
2	0.0909	0.0545	59.95	2	113	103
3	0.0877	0.0554	63.16	3	111	104
4	0.0924	0.0547	59.19	4	130	103
5	0.0937	0.0607	64.78	5	104	99
6	0.0885	0.0541	61.12	6	120	108

TABLE 7

RESULTS OF TAPES PREPARED BY PROCEDURE C

Tape No.	Weight of Tape (g)	Weight of Solution on Tape (g)	Percentage Uptake of Solution	Response Times
1	0.0965	0.0617	63.94	None
2	0.0959	0.0668	69.66	
3	0.0958	0.0680	70.98	
4	0.0965	0.0652	67.56	
5	0.0955	0.0663	69.42	
6	0.0980	0.0697	71.12	

TABLE 8

RESULTS OF TAPES PREPARED BY PROCEDURE D

Tape No.	Weight of Tape (g)	Weight of Solution on Tape (g)	Percentage Uptake of Solution	Tape No.	Response in Seconds: # Half of Tape	Response in Seconds: #A Half of Tape
1	0.0929	0.0583	62.75	1	79	77
2	0.0932	0.0624	66.95	2	86	79
3	0.0960	0.0628	65.41	3	71	None
4	0.0943	0.0591	62.67	4	76	77
5	0.0953	0.0613	64.32	5	83	75
6	0.0946	0.0627	66.27	6	69	69

TABLE 9

RESULTS OF TAPES PREPARED BY PROCEDURE E

Tape No.	Weight of Tape (g)	Weight of Solution on Tape	Percentage Uptake of Solution	Tape No.	Response in Seconds: # Half of Tape	Response in Seconds: #A Half of Tape
1	0.1033	0.0768	74.35	1	108	108
2	0.1035	0.0766	74.01	2	118	123
3	0.1042	0.0726	69.67	3	120	115
4	0.1034	0.0781	75.53	4	123	121
5	0.0985	0.0641	65.08	5	111	120
6	0.1024	0.0705	68.85	6	116	118

TABLE 10

RESULTS OF TAPES PREPARED BY PROCEDURE F

Tape No.	Weight of Tape (g)	Weight of Solution on Tape (g)	Percentage Uptake of Solution	Tape No.	Response in Seconds: # Half of Tape	Response in Seconds: #A Half of Tape
1	0.1033	0.0768	74.35	1	91	82
2	0.1035	0.0766	74.01	2	79	89
3	0.1042	0.0726	69.67	3	81	89
4	0.1034	0.0781	75.53	4	81	80
5	0.0985	0.0641	65.08	5	None	83
6	0.1024	0.0705	68.85	6	85	80

TABLE 11

RESULTS OF TAPES PREPARED BY PROCEDURE G

Tape No.	Weight of Tape(g)	Weight of Solution Before Exp.(g)	Weight of Solution After Exp.(g)	Percentage Uptake of Solution		Tape No.	Loss of Wt. of Solution(g)	Percentage of Weight Loss
				Before Exp.	After Exp.			
1	0.0921	0.0553	0.0472	60.04	51.24	1	0.0081	14.64
2	0.0901	0.0519	0.0437	57.60	48.50	2	0.0082	15.79
3	0.0911	0.0551	0.0474	60.48	52.03	3	0.0077	13.97
4	0.0701	0.0366	0.0279	52.21	39.80	4	0.0087	23.77
5	0.0729	0.0409	0.0325	56.10	44.58	5	0.0084	20.53
6	0.0740	0.0463	0.0394	62.56	53.24	6	0.0069	14.90

TABLE 12

RESULTS OF TAPES PREPARED BY PROCEDURE H

Tape No.	Weight of Tape(g)	Before Exp.(g)	After Exp.(g)	Percentage Uptake of Solution Before Exp.	Percentage Uptake of Solution After Exp.	Loss of Wt. of Solution(g)	% Wt. Loss	Response in Seconds # Half of Tape	Response in Seconds #A Half of Tape
1	0.0803	0.0489	0.0446	60.90	55.54	0.0043	8.79	107	107
2	0.1056	0.0699	0.0651	66.19	61.65	0.0048	6.86	132	133
3	0.0797	0.0513	0.0474	64.37	59.47	0.0039	7.60	104	112
4	0.1053	0.0676	0.0636	64.20	60.40	0.0040	5.91	140	140
5	0.0803	0.0512	0.0466	63.76	58.03	0.0046	8.98	117	120
6	0.1052	0.0667	0.0633	63.40	60.17	0.0034	5.09	121	117
7	0.0801	0.0514	0.0466	64.17	58.18	0.0048	9.33	129	148
8	0.1055	0.0658	0.0592	62.37	56.11	0.0066	10.03	121	132

TABLE 13

RESULTS OF TAPES PREPARED BY PROCEDURE I

Tape No.	Weight of Tape(g)	Weight of Solution on Tape(g)	Percentage Uptake of Solution	Tape No.	Response in Seconds # Half of Tape	Response in Seconds #A Half of Tape
1	0.0850	0.0540	63.25	1	76	70
2	0.0850	0.0540	63.25	2	88	77
3	0.0912	0.0573	62.82	3	76	77
4	0.0912	0.0573	62.82	4	72	69
5	0.0893	0.0560	62.70	5	71	88
6	0.0893	0.0560	62.70	6	77	80
7	0.0961	0.0593	61.70	7	75	75
8	0.0961	0.0593	61.70	8	87	99
9	0.0896	0.0509	56.80	9	58	88
10	0.0896	0.0509	56.80	10	85	76
11	0.0903	0.0519	57.47	11	67	73
12	0.0903	0.0519	57.47	12	75	72

they were all blotted at the same time. The blotting was carried out by placing a dry towel on top of the six tapes, and then applying a gentle, even pressure to remove the excess liquid from them. The two towels with the six tapes between them were then turned over, and the now top "wet" towel was replaced by a fresh one.

This blotting technique was performed until the tapes had been blotted three times on either side. The No. 1 to No. 6 tapes stayed on the "dry" paper towel from 1 minute to 6 minutes. The tapes were then taken up in order and placed in weighing bottles. The same procedure was followed for the tapes used for testing response times except for packaging. These tapes were cut in half and one half packaged before the other.

5.3.2 Preparation Procedure B

In Procedure B, the tapes were soaked in the usual manner, blotted (three times on either side), and placed in weighing bottles or packaged individually for testing. Each tape stayed on the "wet" towel 30 seconds and about the same time on the "dry" towel before being packaged.

5.3.3 Preparation Procedure C

The tapes in Procedure C were prepared like those in Procedure B, but the temperature in the dry box was 6°F higher (about 82°F). Only a weight test was carried out on this set of tapes.

5.3.4 Preparation Procedure D

In Procedure D, the tapes were blotted individually as in Procedure B. After blotting, they were placed on a paper towel and left to stand until all six tapes had been individually soaked and blotted. Each blotted tape was left on the "dry" paper towel for 6 minutes, and then taken up and placed in weighing bottles. A response time test was run on these tapes, too.

5.3.5 Preparation Procedure E

The tapes in Procedure E were prepared like those in Procedure A, except that, after being blotted three times on either side, they were put immediately in an aluminized Mylar bag. The tapes were taken from the bag one at a time and placed in a weighing bottle. The same technique was followed in preparing the tapes to be tested for response time.

5.3.6 Preparation Procedure F

In Procedure F, the tapes were prepared by the same technique used in Procedure E, except that, after blotting, the tapes were put in an aluminized Mylar bag. The bag was then sealed and set aside for 8 minutes. After this time the bag was cut open and the tapes (for the weight test) were removed one at a time and placed in a weighing bottle. The tapes tested for response time were cut in half in the aluminized Mylar bag and packaged individually in order No. 1, No. 1A, No. 2, No. 2A, etc.

5.3.7 Preparation Procedure G

The tapes in Procedure G were prepared like those in Procedure B, i.e., the tapes were soaked and blotted individually. Two new variables were investigated in these experiments. Tapes of different weight were soaked, blotted, and weighed to determine the difference in solution uptake by them. After the tapes were impregnated and weighed, they were taken from their weighing bottles in the N_2 atmosphere dry box and placed on a dry paper towel. The tapes were left on the paper towel exposed to the nitrogen atmosphere for 6 minutes, after which they were returned to their weighing bottles and reweighed.

The exposure of the tapes in the nitrogen was made to find out if there was any relation between the initial weight of the tape and the percentage of weight lost due to evaporation. Only a weight test was made in this procedure.

5.3.8 Preparation Procedure H

The tapes in Procedure H were prepared by the same techniques as those in Procedure G. Eight tapes were prepared by this procedure. After the tapes had been impregnated with the reagent and weighed, they were exposed to the nitrogen atmosphere in the dry box for 10 minutes. The tapes were left in the opened bottles for this period of time. The bottles were then closed and the tapes reweighed to determine the loss of weight. These tapes were packaged and tested for response time after being reweighed. The numbered A-half of the tape was exposed for about 30 seconds longer than the other half of the tape.

5.3.9 Preparation Procedure I

In Procedure I, 12 tapes were prepared like those in Procedure E. The tapes were left on the "wet" towel for different periods of time. The odd-numbered tapes were weighed, and then cut in half and tested for response times. The even-numbered tapes were placed in pockets and tested for response time.

It was apparent from these studies that the number of times the tapes are blotted seriously affects the response time. The standard procedure which finally evolved and is currently used involves blotting the tapes four times on each side with constant pressure. This method of preparation results in uniformly fabricated tapes which respond correctly within the required time limits.

5.4 Exposure of Tapes in Dry Box

The use of hydrazine, a highly volatile material, in the preparation of the chemical tapes raised the question of whether different exposure times inside the dry box would affect the response times. Preliminary investigation indicated that this was indeed the case. To obviate this difficulty, a series of tests relating exposure of the tapes within the dry box to response time were made. The details of this investigation are included in the following paragraphs.

5.4.1 Exposure Test I

The tapes (12) in Exposure Test I were prepared by Procedure E. The tapes were left on the blotting ("wet") towel for decreasing periods of time from 4 minutes 40 seconds to 1 minute. The time for each succeeding tape was reduced by 20 seconds. After being blotted, the tapes were exposed to the nitrogen atmosphere for different lengths of time: tape Nos. 1 and 7 for 1 minute; Nos. 2 and 8 for 2 minutes; Nos. 3 and 9 for 4 minutes; Nos. 4 and 10 for 6 minutes; Nos. 5 and 11 for 10 minutes; and Nos. 6 and 12 for 15 minutes. After exposure, each pair of tapes was sealed in an aluminized Mylar bag for 15 minutes. The tapes were then cut in half in the bag and packaged in order (Nos. 1 and 7, etc.) for response time testing.

5.4.2 Exposure Test II

In Exposure Test II, 12 tapes were prepared by Procedure E in the order of Nos. 1, 7, 2, 8, etc. The No. 1 tape was on the "wet" towel for 4 minutes 40 seconds; No. 7 for 4 minutes 20 seconds; No. 2 for 4 minutes; etc. The tapes were left on the "wet" towel for periods of time decreasing by 20 seconds for each succeeding tape. Tape Nos. 1 to 6 were placed on a dry towel and exposed to the nitrogen atmosphere for 4 minutes, while tape Nos. 7 to 12 were exposed for 10 minutes. The tapes were sealed in an aluminized Mylar bag for 6 minutes after exposure. The tapes were then cut in half in the bag and packaged in badges (in the order from Nos. 1 and 1A to Nos. 6 and 6A, from Nos. 7 and 7A to Nos. 12 and 12A). Tape Nos. 2, 4, 8, 10, and their #A halves were tested for response time on the day of preparation. The remainder of the tapes were tested under the same conditions 3 days later.

5.4.3 Exposure Test III

The tapes in Exposure Test III were handled in the same manner as those in Exposure Test II. They were prepared in the order of Nos. 1, I, 2, II, etc. Tape Nos. 1 to 6 were on the dry towel for 4 minutes and tape Nos. I to VI were exposed to nitrogen on the dry towel for 10 minutes. The tapes were cut in half in the aluminized Mylar bag and packaged (in order from No. 1 to No. 6 and from No. I to No. VI) for response time tests. They were tested on the day of preparation.

5.4.4 Exposure Test IV

In addition to the three exposure tests above, a test similar to Exposure Test I was run on four types of tapes. A dozen of each type of tape (2, 4, 6, and 8 mm) was prepared by Procedure E. The tapes were 9.75% hydrazine-Crystal Violet tapes, 12.45% hydrazine-Crystal Violet tapes, 6.1% hydrazine-Basic Fuchsin tapes, and 7.5% hydrazine-Basic Fuchsin tapes. Two tapes of each of these sets of tapes were exposed to the nitrogen atmosphere in the dry box for 0, 4, 8, 12, 16, and 20 minutes. The four types of tapes (9.75%, 12.45%, 6.1%, and 7.5% N_2H_4) were exposed to 2-, 4-, 6-, and 8-mm partial pressures of CO_2, respectively.

The results of Exposure Tests I, II, and III are shown in tables 14 through 16, and a graph of the response times of Exposure Test I is shown in figure 6. The tapes were handled as stated in paragraph 5.4.2.

Figures 7 through 10 show the results of the exposure time to nitrogen versus response time of four levels of tapes prepared by Procedure E. Each point plotted on the graph is the average response time of two tapes or four halves of tapes.

The graph shown in figure 11 shows the response times of the same levels of tapes (9.75%, 12.45%, 6.10%, and 7.5% hydrazine) exposed for 16, 10, 18, and 12 minutes, respectively, and exposed to all four levels of carbon dioxide concentration (2-, 4-, 6-, and 8-mm partial pressures). In all tests the Crystal Violet tapes were compared to a 1:10 Crystal Violet reference, while the Basic Fuchsin tapes were compared to a 1:32 Fuchsin reference.

It is seen from the information gained on the effects of exposure of the tapes in the dry box to nitrogen that long exposure differences between the first and last tapes soaked lead to nonuniform tapes. For this reason, the tapes which are prepared 12 at a time are stored in an aluminized Mylar bag immediately after blotting, unless a controlled exposure is required to produce a certain level of response. The temperature of the dry box is also controlled, since temperature changes within the environment will also affect the response time by changing the rate of evaporation of hydrazine.

5.4.5 <u>Exposure Time of Tapes to Nitrogen in Dry Box in Relation to Weight of Solution Lost.</u>

In the tests of exposure times of tapes to nitrogen in the dry box in relation to response times, the tapes appeared to be losing some solution by

TABLE 14

RESULTS OF EXPOSURE TEST I

Tape No.	Response in Seconds # Half	Response in Seconds #A Half	Tape No.	Response in Seconds # Half	Response in Seconds #A Half
1	96	88	7	80	91
2	73	73	8	80	70
3	70	61	9	50	59
4	None	54	10	62	62
5	40	50	11	41	45
6	45	38	12	35	38

TABLE 15

RESULTS OF EXPOSURE TEST II

Tested 10/16/64			Tested 10/19/64		
Tape No.	Response in Seconds # Half	Response in Seconds #A Half	Tape No.	Response in Seconds # Half	Response in Seconds #A Half
2	61	52	1	53	62
4	66	58	3	52	42
8	52	49	5	59	60
10	50	51	6	62	63
			7	50	55
			9	54	46
			11	43	43
			12	53	48

TABLE 16

RESULTS OF EXPOSURE TEST III

Exposed 4 Minutes			Exposed 10 Minutes		
Tape No.	Response in Seconds # Half	Response in Seconds #A Half	Tape No.	Response in Seconds # Half	Response in Seconds #A Half
1	73	84	I	64	66
2	77	60	II	60	55
3	71	64	III	59	61
4	82	78	IV	59	69
5	67	67	V	66	71
6	78	70	VI	56	60

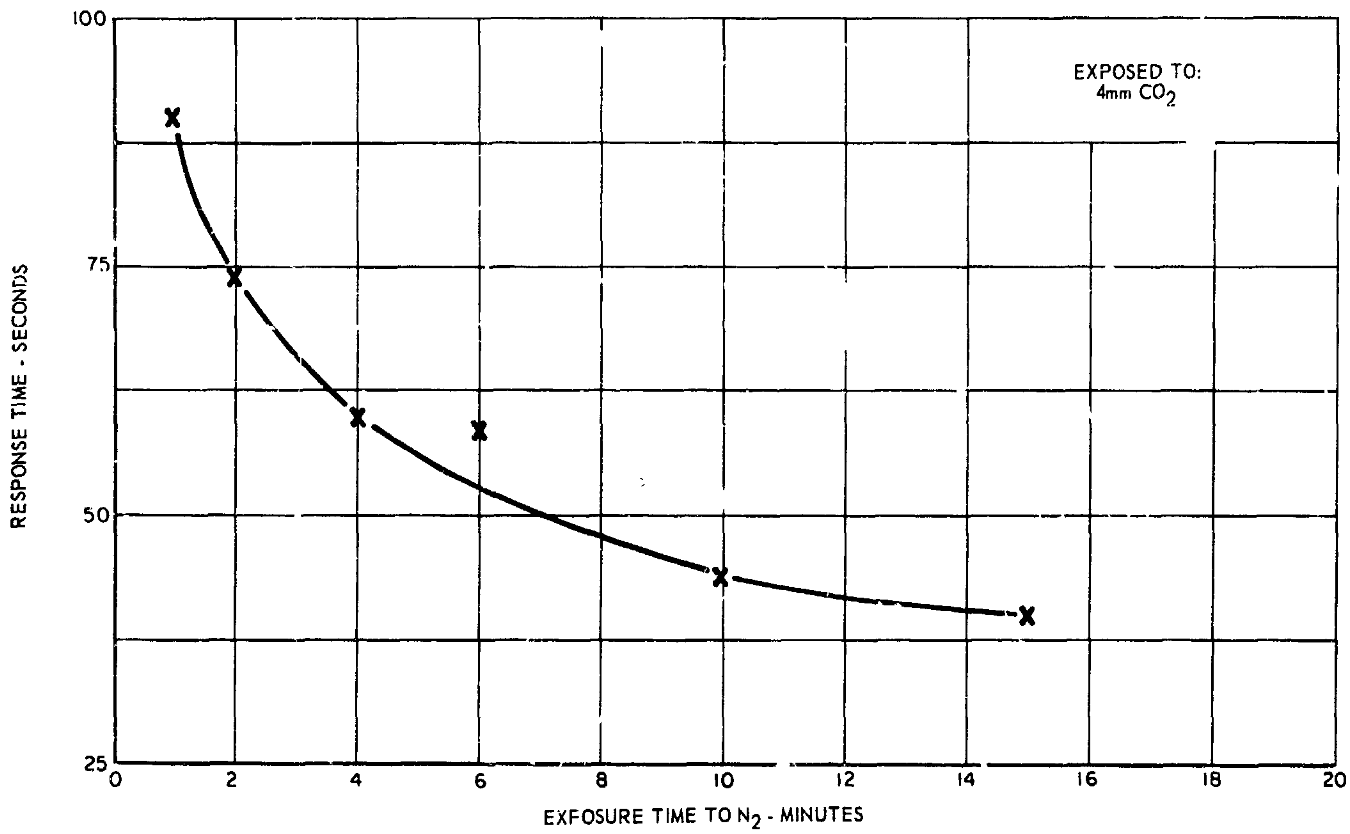


Figure 6. Exposure Time to N_2 Versus Response Time

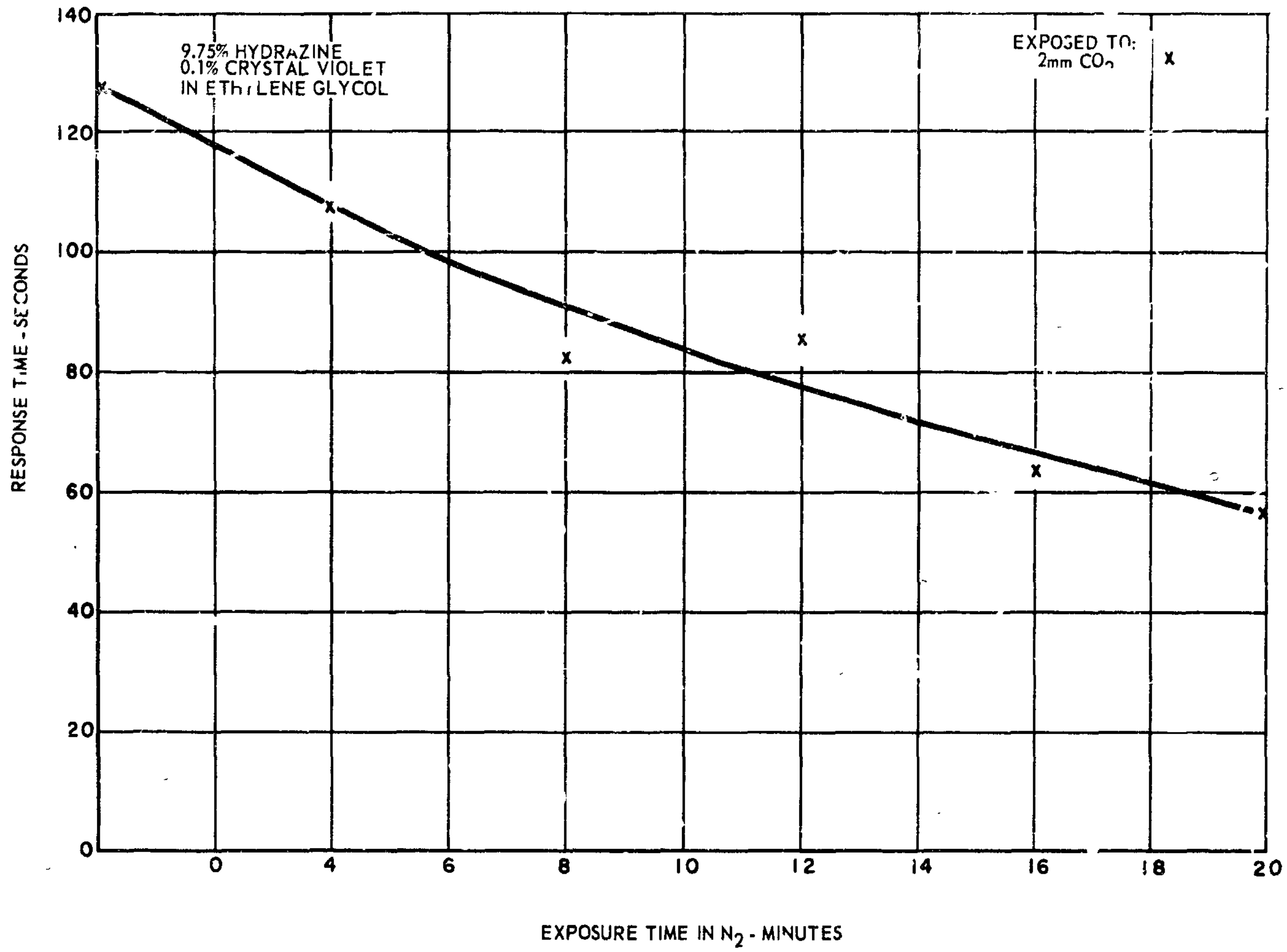


Figure 7. Exposure [illegible] N_2 Versus Response Time (9.75% Hydrazine-Crystal Violet Tape)

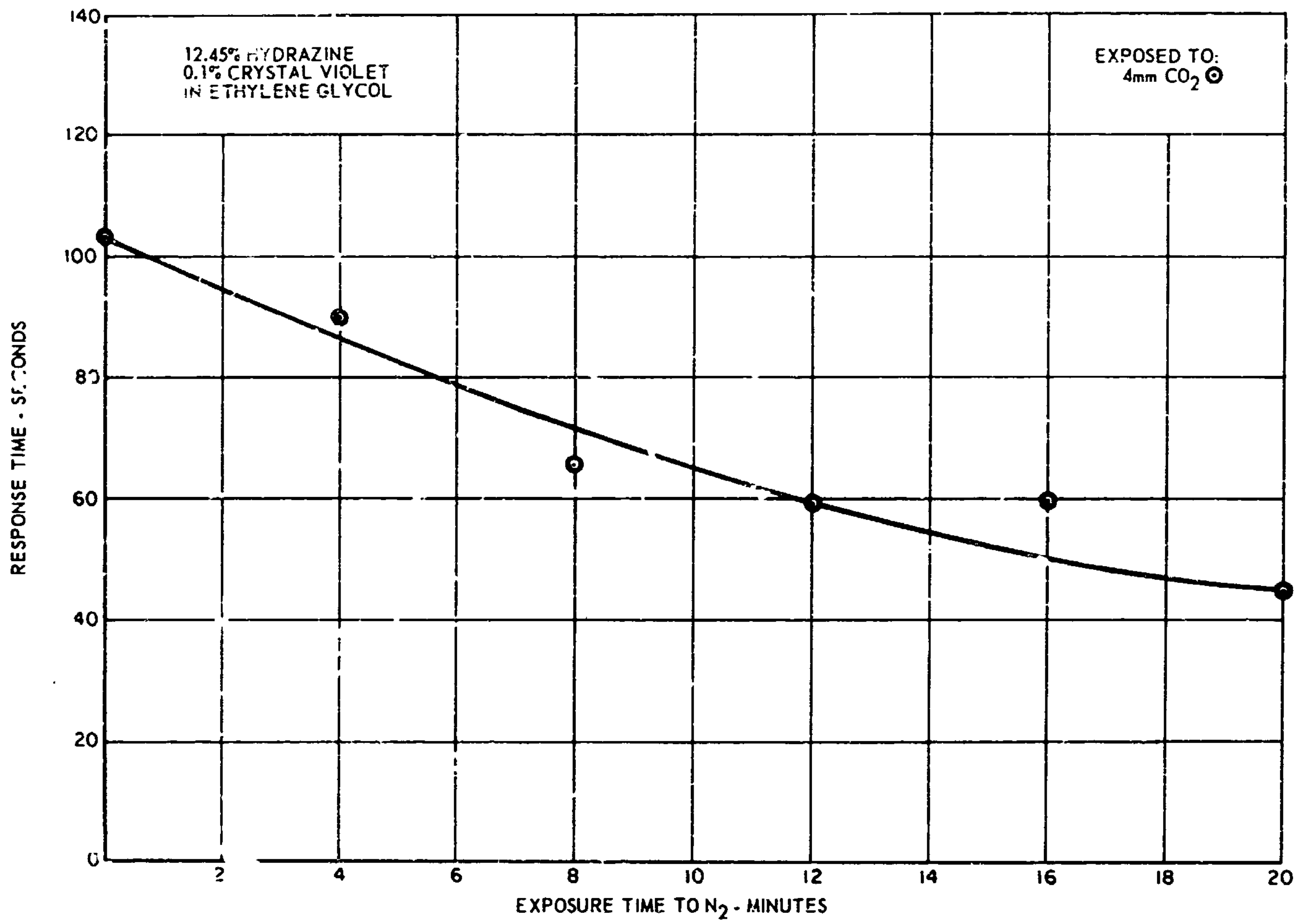


Figure 8. Exposure Time to N_2 Versus Response Time (12.45% Hydrazine-Crystal Violet Tape)

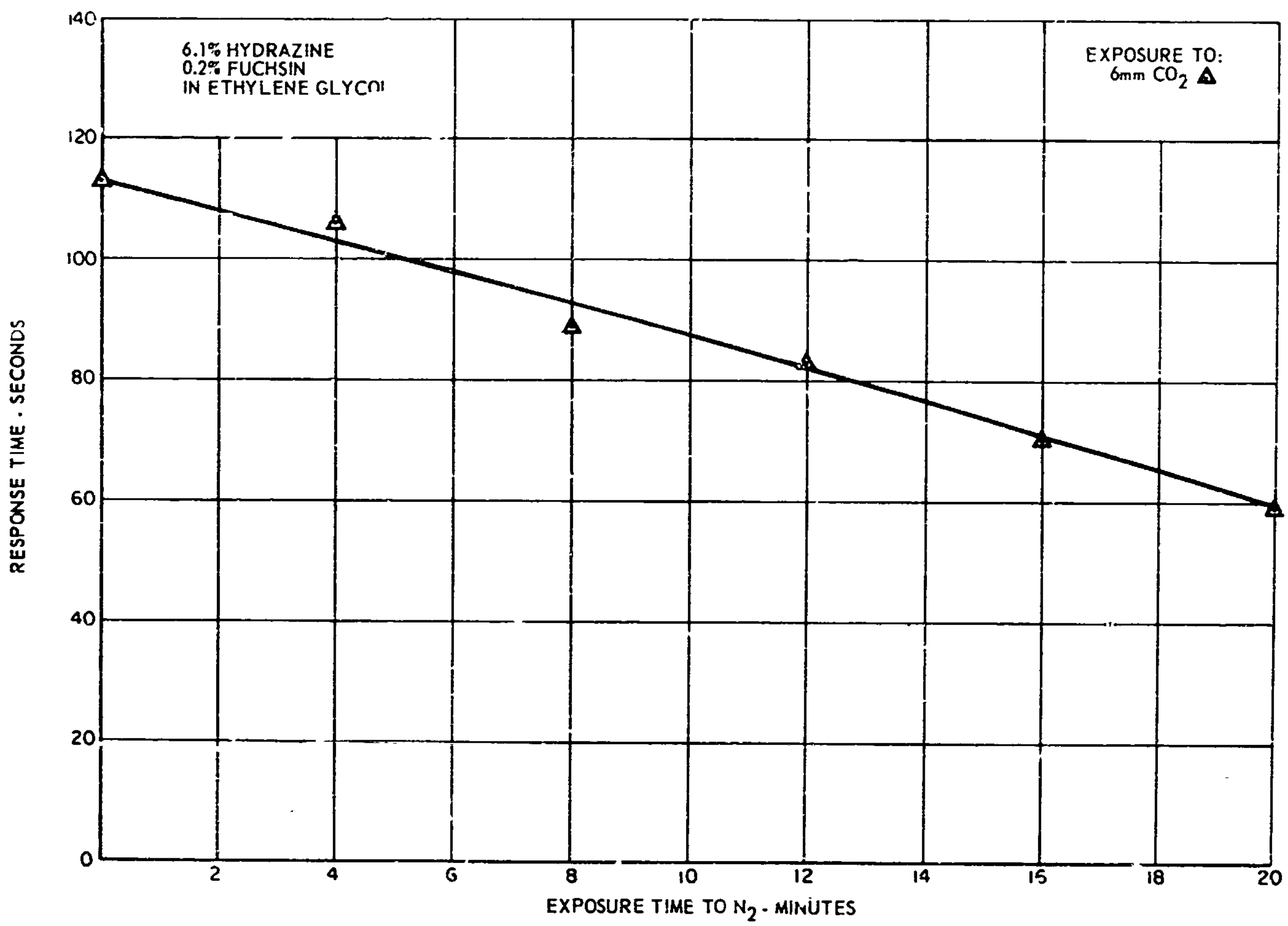


Figure 9. Exposure Time to N_2 Versus Response Time (6.10% Hydrazine-Basic Fuchsin Tape)

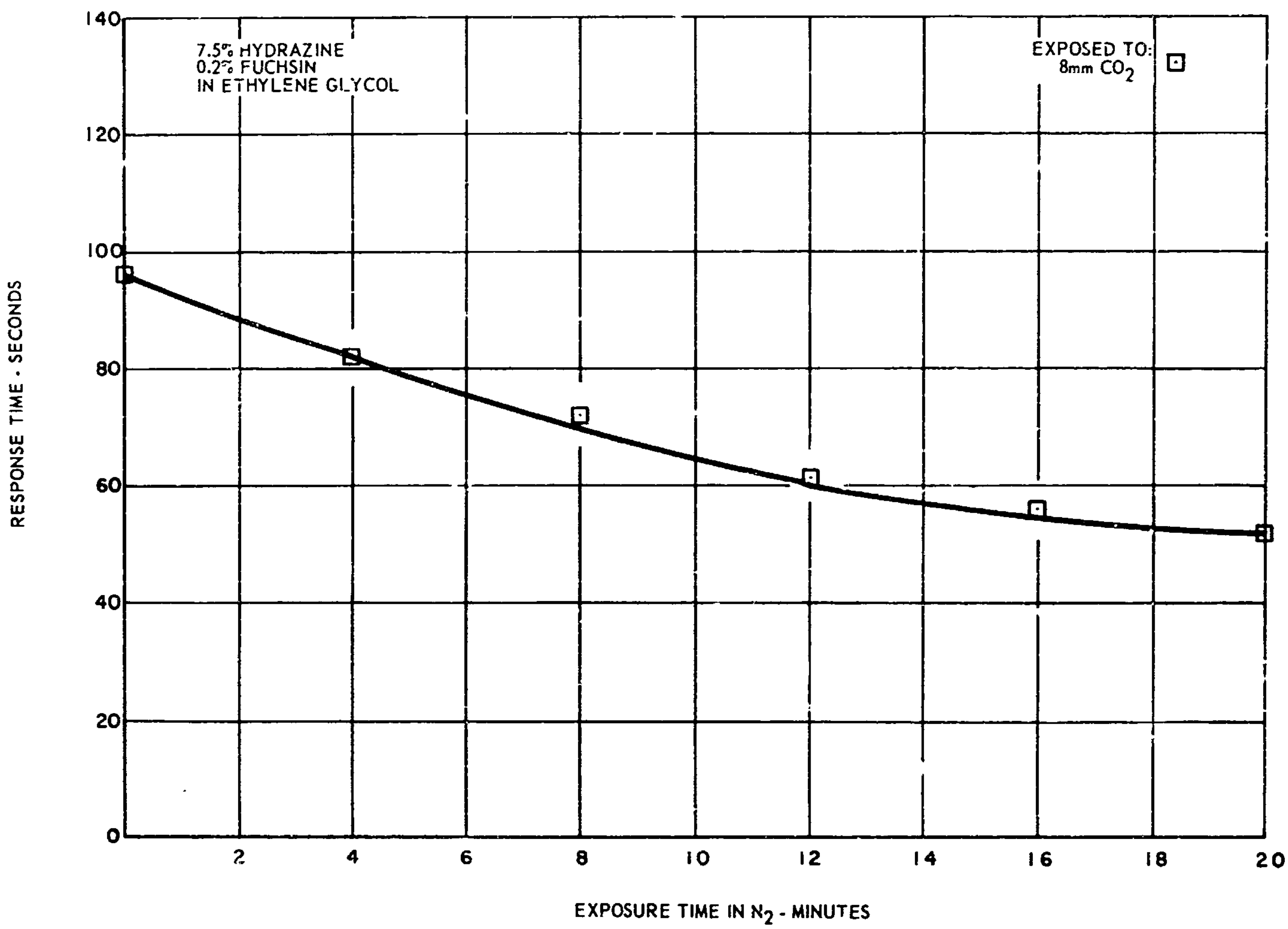


Figure 10. Exposure Time to N_2 Versus Response Time (7.50% Hydrazine-Basic Fuchsin Tape)

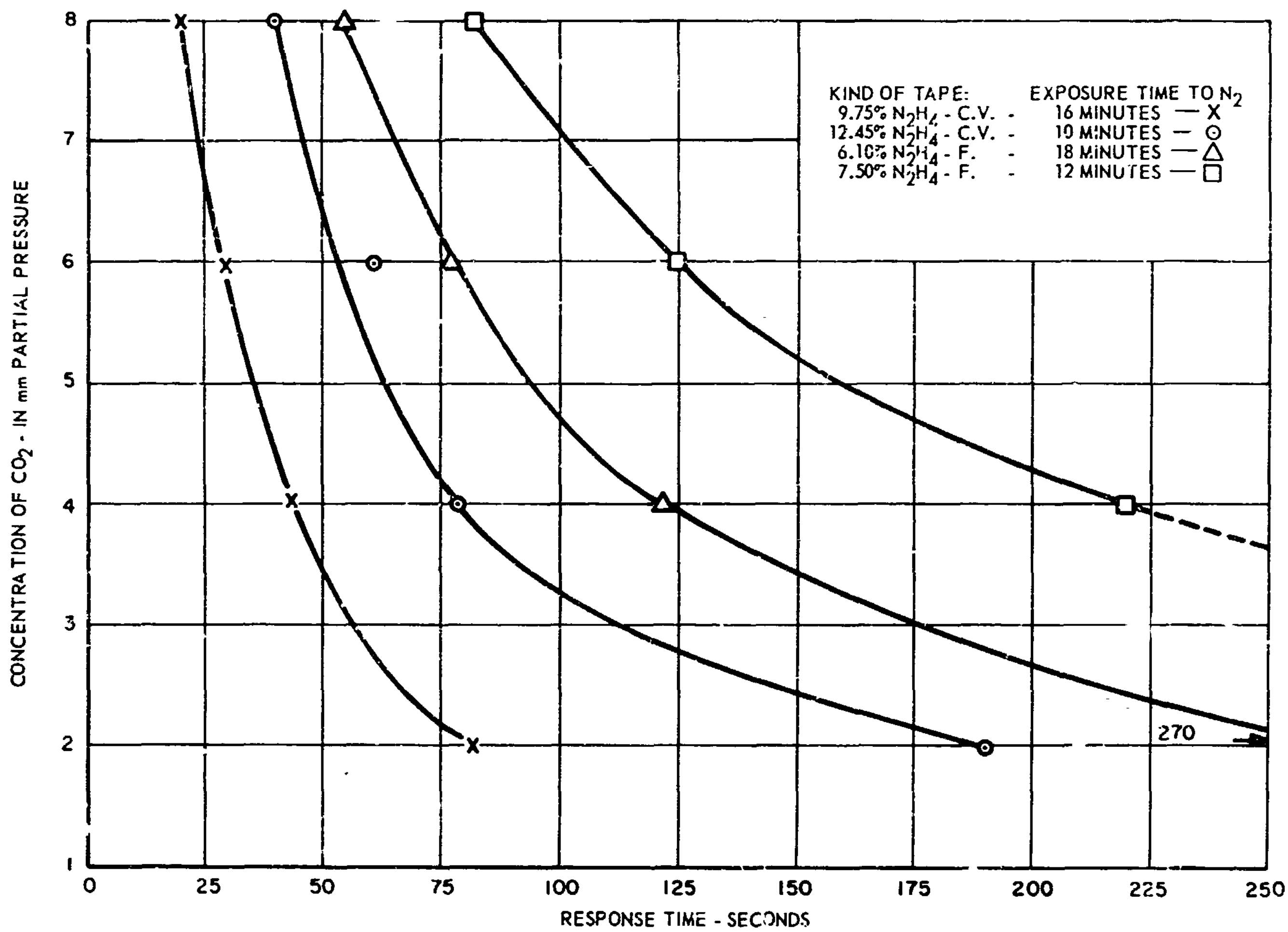


Figure 11. Response Time of Tapes at Different CO_2 Concentrations

evaporation. Some tests were carried out in attempts to verify that the evaporation of solution was occurring. First, two tapes of approximately the same weight were soaked for 1 minute each in two different solutions. One tape was impregnated with a 12.50% hydrazine-Crystal Violet-ethylene glycol solution and the other tape was dipped only in ethylene glycol. Both tapes were weighed to determine the weight of solution taken up by each. The tapes were then placed in the dry box and exposed to the nitrogen atmosphere for 6 minutes, returned to their bottles, and reweighed to find the loss in weight of both solutions.

Another test was carried out with a single tape in which the weighed tape was soaked in the same 12.50% hydrazine-Crystal Violet solution for 1 minute, blotted three times on either side, placed in a weighing bottle, and reweighed. After this initial weighing, the tape was exposed to the nitrogen atmosphere for 1, 2, 4, 6, 10, 15, and 30 minutes, and weighed after each of the exposures.

The results observed in each of three exposure time versus loss of weight tests are shown in tables 17 and 18. Figure 12 is a plot of the results obtained from the third or extended exposure time test. Figure 13 shows the relation of change in response time to change in weight with respect to exposure time in nitrogen. In the variable $\Delta R/\Delta W$, ΔR is the change in response time with respect to exposure time to nitrogen; and ΔW is the change in weight with respect to exposure time.

5.5 Method of Preparing and Packaging CO_2 Tapes

The following paragraphs contain step-by-step descriptions of how the carbon dioxide detection tapes are prepared and packaged.

TABLE 17

RESULTS OF EXPOSURE TIME VERSUS LOSS OF WEIGHT TEST

Tape Soaked in Hydrazine-Crystal Violet Sol.		Tape soaked in Ethylene Glycol	
Original wt. of tape	- 0.0970 g.	Original wt. of tape	- 0.0979 g.
Wt. of sol. before exposure to N_2	- 0.0717 g.	Wt. of sol. before exposure to N_2	- 0.0636 g.
Wt. of sol. after exposure to N_2	- 0.0602 g.	Wt. of sol. after exposure to N_2	- 0.0559 g.
Loss of wt. of sol.	- 0.0115 g.	Loss of wt. of sol.	- 0.0077 g.

TABLE 18

RESULTS OF EXPOSURE TIME VERSUS LOSS OF WEIGHT TEST

Minutes Exposed to N_2	Weight Change (g.)	Weight of Solution (g.)
0	--	0.0601
1	0.0009	0.0592
2	0.0017	0.0584
4	0.0022	0.0579
6	0.0041	0.0560
10	0.0060	0.0541
15	0.0078	0.0523
30	0.0118	0.0483

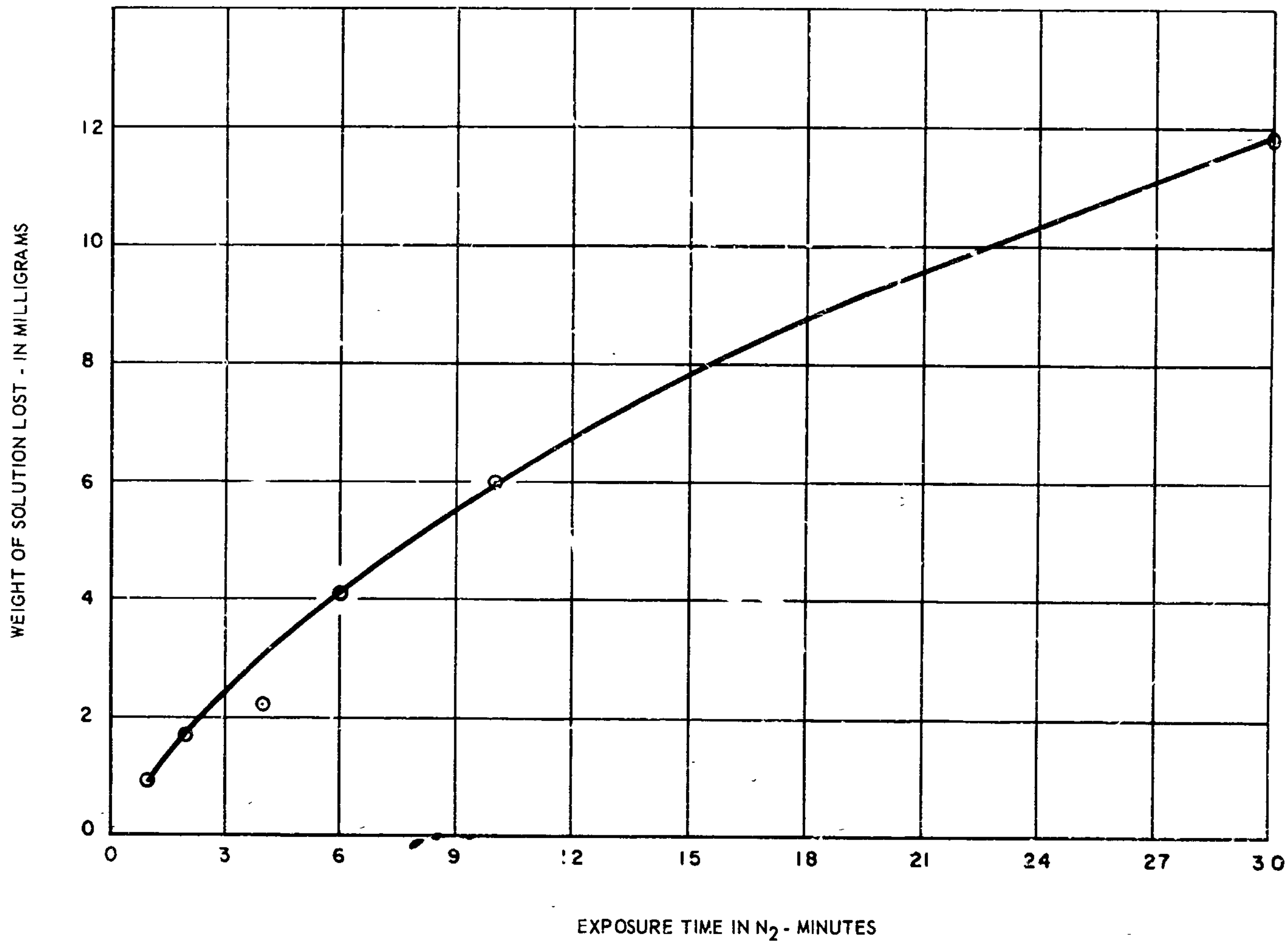


Figure 12. Exposure Time in N_2 Versus Weight of Solution Lost

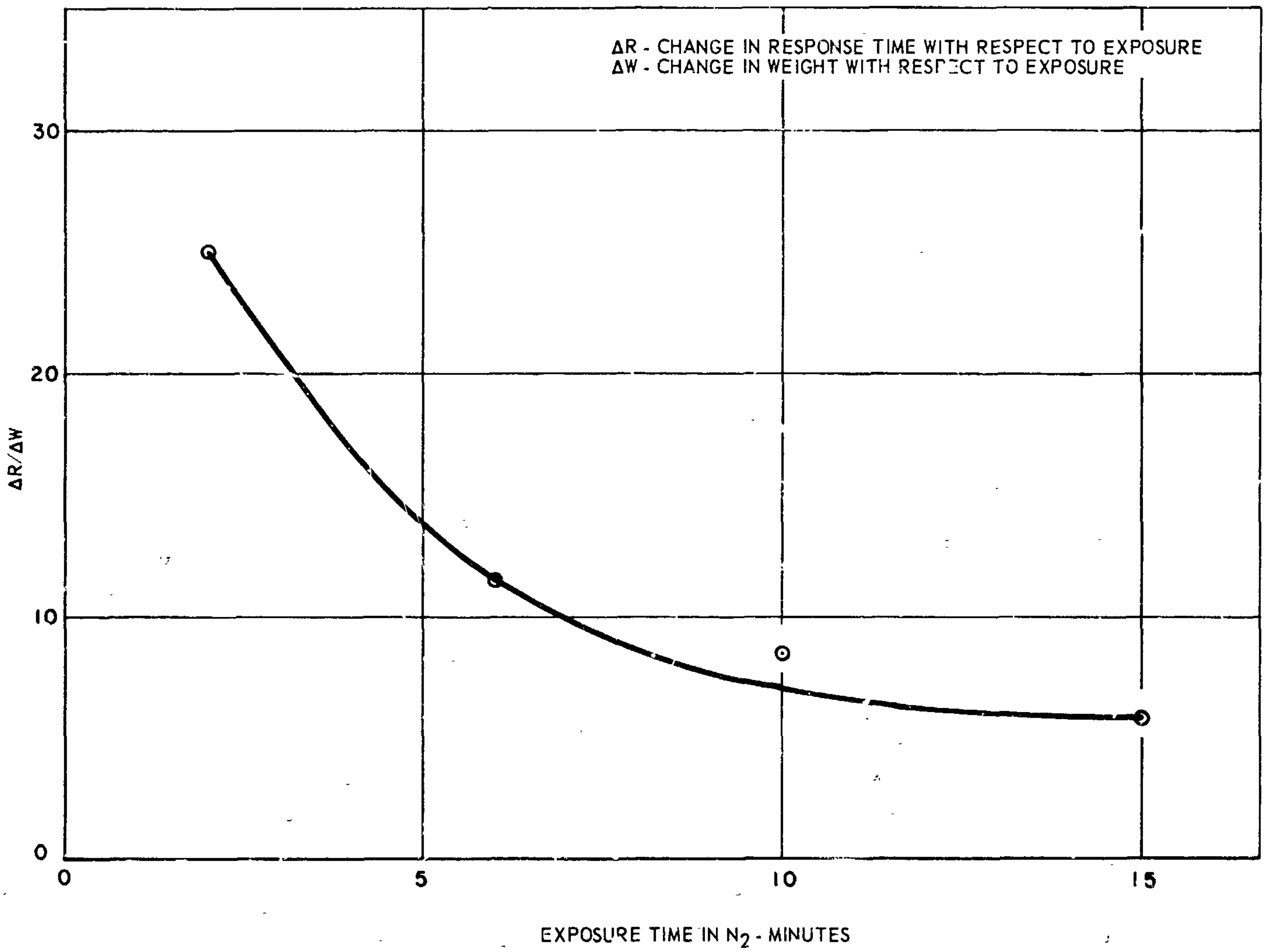


Figure 13. Change in Response Time and Loss of Weight of Solution with Respect to Exposure Time in N_2

5.5.1 Preparation of Tapes

The tapes are prepared as follows:

a. Whatman No. 541 filter paper is cut into strips 5/8 inch wide by 3 inches long and, for convenience, arranged into sets of 12.

b. For preparation of tapes sensitive to 2 and 4 mm of CO_2, a 0.5% w/v master solution of Crystal Violet in ethylene glycol is prepared. This solution is used for the preparation of the 0.1% Crystal Violet solutions in steps f and g.

c. For preparation of tapes sensitive to 6 and 8 mm of CO_2, a 0.5% w/v master solution of Basic Fuchsin in ethylene glycol is prepared. This solution is used for the preparation of the 0.2% Basic Fuchsin solutions in steps h and i.

d. Make a hydrazine solution in ethylene glycol containing approximately 30% hydrazine.

e. Determine titrimetrically with N/10 potassium iodate solution the exact concentration of hydrazine in the solution prepared according to step d.

f. The solution for preparation of tapes sensitive to 2-mm partial pressure CO_2 consists of 0.1% w/v Crystal Violet solution (20% of solution made according to step b), containing 9.75% w/v hydrazine (appropriate amount of hydrazine solution made and standardized according to steps d and e) together in ethylene glycol (tape R254858-1).

g. The solution for preparation of tapes sensitive to 4-mm partial pressure CO_2 consists of 0.1% w/v Crystal Violet solution (20% w/v hydrazine solution made according to step b), containing 13.00% w/v hydrazine (appropriate amount of hydrazine solution made and standardized according to steps d and e) in ethylene glycol (tape R254859-2).

h. After the 2- and 4-mm tapes, the solution for the 6- and 8-mm tapes are also made up in ethylene glycol. The mixture for the 6-mm tapes consists of 0.2% w/v Basic Fuchsin solution (40% w/v of solution made according to step c) with 6.1% w/v hydrazine (appropriate amount of hydrazine solution in ethylene glycol made according to steps d and e) (tape R254858-3).

i. The solution for preparing the 8-mm tapes consists of 0.2% w/v Basic Fuchsin in ethylene glycol (40% w/v solution made following instructions of step c) with 8.00% w/v hydrazine (calculated appropriate amount of hydrazine solution made and controlled following instructions of steps d and e) (tape R254858-4).

j. Each of the above four preparative solutions is made immediately prior to use.

k. All materials are placed in a dry box at 78° to 82°F, 20% to 25% r.h., and with a flow of nitrogen at 10 liters/minute.

l. Approximately 50 ml of reagent are placed in a 6-inch-diameter glass Petri dish.

m. Three tapes are inserted into this solution, one at a time, in intervals of 20 seconds each. The total immersion time for each tape is 1 minute. The tapes are removed at 20-second intervals and, as each tape is removed, another tape is inserted until 12 tapes have been soaked in the solution for 1 minute each.

n. As each tape is removed, it is allowed to drain for 5 seconds, after which it is placed on a stack of five clean paper towels. After this operation has been performed with the entire batch of 12 tapes, and the final tape has been placed on the towels, a waiting period of 2 minutes is required before preceeding to the next step.

o. Cover with four additional paper towels and invert the stack of towels (step i) containing the tapes in the middle.

p. Remove the five top towels, remove the towel immediately above the tapes, place the four fresh towels on the tapes, and place plate weighing 2.3 kg on the towels for 15 seconds.

q. Remove the weight, remove the towel touching the tapes, invert the stack of towels, and remove the towel over the tapes. Place the weight on the six towels for 15 seconds. Rotate the three remaining towels on either side of the tapes and place the weight on the towels until three changes of towels have been performed.

r. The tapes are left exposed on the towels inside the dry box for the following periods of time for each concentration level (X is predetermined for each lot of solution):

(1) 2 mm - X minutes.

(2) 4 mm - X minutes.

(3) 6 mm - X minutes.

(4) 8 mm - X minutes.

s. All tapes of similar sensitivity are then placed in an aluminized Mylar bag and sealed. They may be stored at ambient conditions until they are ready to be packaged.

5.5.2 Preparation of Reference Strips

The reference strips are prepared as follows:

a. Reference colored strips are cut to 3/4 inch by 1-1/8 inches and punched prior to dipping.

b. A Crystal Violet reference solution, consisting of 1 part of the 0.5% w/v Crystal Violet dilution plus 35 parts of ethylene glycol, is used to prepare reference strips for 2- and 4-mm badges. No hydrazine is added.

c. The reference strips are dipped into the solution for 30 seconds and blotted.

d. A Basic Fuchsin reference solution, consisting of 1 part of 0.5% w/v Basic Fuchsin solution to 32 parts ethylene glycol, is used to prepare the reference strips for the 6- and 8-mm badges. No hydrazine is added.

e. These reference strips are dipped into the solution for 30 seconds and blotted.

f. The blotted-dry reference tapes are inserted in the proper pockets of the badges and sealed.

5.5.3 Packaging of CO_2 Detection Tapes

Packaging of the CO_2 detection tapes is accomplished as follows:

a. The badges and test tapes are placed within the dry box at the former conditions, and the test tapes are cut into three 1-inch lengths. Four of these 1-inch tapes from each half dozen of 3-inch tapes are tested for response time at the proper level.

b. Each tape is inserted in its proper pocket in the badge and freshly cut edge first, in reverse order; i.e., 8, 6, 4, and 2 mm.

c. The front cover tab is folded down over the supporting tab and the top of the rear pocket is sealed.

d. These seals are then resealed on the large impulse sealer.

e. Each detector is leak-tested by placing it in a 1-mm vacuum for 36 hours. The detector is then inspected for faded reference strips, which indicate leaks.

f. The badges are cleaned and packed in a second bag, and then into a third container which is transparent.

6. RELIABILITY STUDIES OF TAPES

It was known at the beginning of the project that the reproducibility of readings would have to be evaluated carefully so that the usefulness of the completed badges would be known. For this reason, a number of studies concerning their reproducibility, the reader's error, and the effect of environmental influences were made, and the limitations of the expected error became known.

6.1 Reproducibility of Tapes and the Reader's Error Studies

A 1-month reliability study was made on 168 tape badges. These tape badges were stored under room temperature, pressure, and relative humidity. Any tape not giving the desired response within ±10 seconds of the expected response time was considered a complete failure. A reliability figure was also obtained for the ±10% range of the expected value.

One person prepared all the badges, 48 badges being prepared on two separate days and 36 badges being prepared on two separate days. The 48 made on the first day were labeled Set No. 1; the 48 made on the second day were labeled Set No. 2; the 36 made on the third day were labeled Set No. 3; and the 36 made on the fourth day were labeled Set No. 4. Twelve badges were drawn at random from each set and combined to form Group No. 1. The procedure was repeated to form Group Nos. 2, 3, and 4. A person other than the badge maker formed the four groups. The four groups were tested by four testers, trained in reading CO_2 detection tapes. The testers did not know the failure time, thus eliminating testing bias. The badges from the four sets comprising a group were randomly given to the tester for testing, eliminating possible variation in the sets due to tester improvement.

From this type of program, the variations due to badge preparation techniques and variations due to testers were determined, and reliability controls were established.

The design explained above is shown in the following tabulation:

	Tester			
Set No.	I	II	III	IV
1	12 badges	12 badges	12 badges	12 badges
2	12 badges	12 badges	12 badges	12 badges
3	12 badges	12 badges	12 badges	12 badges
4	12 badges	12 badges	12 badges	12 badges

The data obtained from [illegible] experiment are found in table 19, and a breakdown of the data is shown in table 20.

An analysis of the data indicates that some significant differences exist between tester accuracies, between tester responses, and between tapes prepared on separate days. Based on an analysis of the responses of testers I and II only, the following magnitude of errors was found:

Standard deviation within days	= 7.8 seconds
Standard deviation between tapes prepared on separate days	= 4.8 seconds
Standard deviation between responses of testers	= 3.0 seconds

A second reliability study was performed after the initial study pointed up the differences that existed. It was designed to determine whether the differences which were found in the first study had been eliminated.

TABLE 19

RELIABILITY STUDY

Testers	8 Sept. 64		9 Sept. 64		10 Sept. 64		11 Sept. 64	
	60	71	74	64	83	77	74	73
	68	69	71	69	73	86	87	60
Tester I	66	64	62	63	93	86	84	63
	58	58	67	57	80	81	91	73
	64	65	73	100	79	87	64	69
	59	61	81	63	73	81	75	63
	77	69	70	73	70	68	52	55
	65	59	82	73	60	78	57	69
Tester II	58	52	75	66	67	75	57	61
	73	73	63	58	72	85	62	46
	60	68	64	64	70	59	55	72
	72	59	67	75	78	70	60	56
	58	94	84	87			60	88
	68	82	88	90			76	61
Tester III	63	77	85	69			83	68
	73	79	75	81			64	61
	76	72	74	75			74	69
	81	93	78	81			72	70
			84	84	80	81	61	82
			75	81	74	90	92	76
Tester IV			50	85	79	85	77	72
			81	67	72	74	87	102
			80	78	114	77	89	62
			102	72	74	73	80	79

Notes which apply:

Response is in seconds.

Solution and tapes were prepared by same person.

Tapes were tested at 4 mm CO_2.

Solution was 9.5% hydrazine and 0.1% Crystal Violet.

TA

RELIABILITY

Preparatic

Testers	8 Sept. 64	9 Sept. 64
Tester I	$X_{1,1} = 63.6$ $S_o = 4.4$ Rng=58-71	$X_{1,2} = 70.3$ $S_o = 11.4$ Rng=57-100
Tester II	$X_{2,1} = 65.4$ $S_o = 7.8$ Rng=52-77	$X_{2,2} = 70.0$ $S_o = 5.7$ Rng=63-82
Tester III	$X_{3,1} = 76.2$ $S_o = 10.7$ Rng=58-94	$X_{3,2} = 80.6$ $S_o = 6.5$ Rng=69-90
Tester IV	$X_{4,1} = (75.0)^*$	$X_{4,2} = 78.3$ $S_o = 12.3$ Rng=50-102
	$X_{.1} = 68.4$	$X_{.2} = 74.8$

(1) $X_{T,D}$ = "T" subscript stands for tester; "D" subscript s

(2) $X_{.,D}$ = Mean of all responses on particular day.

(3) $X_{T,.}$ = Mean of all responses for a particular tester.

(4) S_o = Standard error within days (includes error of te

(5) S_1 = Standard error of tester over 4 days (or 3 days)

(6) $(\ )^*$ = Estimates of missing values.

BLE 20

: STUDY ANALYSIS

n Days

	10 Sept. 64	11 Sept. 64	
	$X_{1,3} = 81.6$ $S_o = 5.9$ Rng=73-93	$X_{1,4} = 73.0$ $S_o = 10.0$ Rng=60-91	$X_{1.} = 72.1$ $S_1 = 8.4$
	$X_{2,3} = 71.0$ $S_o = 7.4$ Rng=59-85	$X_{2,4} = 58.5$ $S_o = 5.6$ Rng=46-72	$X_{2.} = 66.2$ $S_1 = 6.7$
	$X_{3,3} = (83.3)^*$	$X_{3,4} = 70.5$ $S_o = 7.4$ Rng=60-88	$X_{3.} = 75.8$ $S_1 = 8.4$
	$X_{4,3} = 81.1$ $S_o = 11.9$ Rng=72-114	$X_{4,4} = 79.9$ $S_o = 11.8$ Rng=61-102	$X_{4.} = 79.8$ $S_1 = 12.0$
	$X_{.3} = 77.9$	$X_{.4} = 70.5$	

tands for day of preparation.

ster and tapes prepared on same day).

).

A total of 192 test tapes was prepared for the study. All of the tapes were made under identical environmental conditions, using a 6.1% Fuchsin-hydrazine system and tested at a 6-mm partial pressure of CO_2.

Two people prepared a total of 64 test tapes on each of three separate days: Preparer 1 making 48 tapes and Preparer 2 making 16 tapes. Tapes were prepared and tested on the same day. The 48 tapes made by Preparer 1 were randomly divided among three testers for determination of response times. The 16 tapes made by Preparer 2 were tested for response by one of the testers. The tapes made on each day were numbered from 1 to 64 in the order in which they were made.

The purpose of the experiment was fivefold:

a. To determine the variation in response time for different testers.

b. To determine whether identical tapes could be prepared on separate days.

c. To determine whether identical tape units could be prepared by different persons.

d. To determine whether a response to time of exposure trend was still indicated.

e. To establish some estimate of response mean and confidence limits for the existing system.

The responses of the 192 tapes tested in the reproducibility study are shown in table 21. A breakdown of these data is available in table 22.

The analysis of the experimental data was separated into two parts. The initial analysis dealt with the data _in toto_, and a second analysis

TABLE 21

DATA FROM RELIABILITY STUDY NO. II

	Preparer No. I						Preparer No. II	
	Tester No. I		Tester No. II		Tester No. III		Tester No. I	
Day Number 1	80	61	119	120	61	71	58	65
	60	71	133	93	67	83	62	72
	65	64	92	94	68	79	70	68
	76	56	86	89	59	92	68	65
	72	74	89	109	63	76	65	63
	58	80	102	114	77	69	64	70
	67	72	87	99	66	63	58	69
	64	68	130	101	70	69	65	76
Day Number 2	58	66	77	113	70	62	73	57
	91	68	94	87	72	71	63	71
	91	66	83	78	64	63	74	59
	58	68	87	98	67	68	60	74
	70	58	83	87	57	67	57	67
	68	67	94	90	70	74	70	74
	54	70	78	113	77	68	60	67
	62	68	113	98	55	68	70	65
Day Number 3	59	58	80	76	62	61	58	61
	61	56	93	95	55	46	64	64
	61	60	79	74	61	55	59	55
	56	66	103	91	56	57	59	74
	59	60	78	81	57	56	59	64
	68	60	68	101	56	63	62	67
	52	55	67	93	52	59	69	56
	63	63	92	85	55	59	61	60

(1) Tapes were tested at 6 mm of CO_2.

(2) Response time is in seconds.

TABLE 22

DATA FROM RELIABILITY STUDY NO. II

	Preparer No. I			Preparer No. II
	Tester No. I	Tester No. II	Tester No. III	Tester No. I
Test Day No. 1	$\bar{X} \hat{=} 68$ Range 56-80 $S^* = 7.5$	$\bar{X} \hat{=} 104$ Range 86-133 $S \hat{=} 15.5$	$\bar{X} \hat{=} 70.2$ Range 59-83 $S \hat{=} 7.4$	$\bar{X} \hat{=} 66$ Range 58-76 $S \hat{=} 5.0$
Test Day No. 2	$\bar{X} \hat{=} 68$ Range 54-91 $S \hat{=} 10.4$	$\bar{X} \hat{=} 92$ Range 77-113 $S \hat{=} 12.3$	$\bar{X} \hat{=} 67$ Range 55-77 $S \hat{=} 5.8$	$\bar{X} \hat{=} 66$ Range 57-74 $S \hat{=} 5.9$
Test Day No. 3	$\bar{X} \hat{=} 60$ Range 52-68 $S \hat{=} 4.0$	$\bar{X} \hat{=} 85$ Range 67-103 $S \hat{=} 10.6$	$\bar{X} \hat{=} 57$ Range 46-68 $S \hat{=} 4.4$	$\bar{X} \hat{=} 62$ Range 55-74 $S \hat{=} 4.7$

*S = sample standard deviation.

Tapes tested at 6 mm of CO_2.

dealt with selected portions of the data. The second analysis was required to give a fairly accurate measure of system errors.

The initial analysis indicated that, as found in the first reliability study, a significant difference existed between responses of different testers and between responses of tapes prepared on different days. However, the curing time of the tape to response time trend found in earlier studies had been removed. This problem was alleviated by using standard curing conditions. The analysis also indicated that no differences could be detected between tape preparers.

The second analysis of the data utilized only the responses of Testers I and III. The responses of Tester II were eliminated in this analysis because of the nonconformity with the other two testers, indicating a significant tester variation. The estimates of system errors based on this analysis are:

a. 6.8 seconds - Experimental error.

b. 0.4 second - Error between testers within days.

c. 5.8 seconds - Error between days.

It is seen that the error between testers found in the <u>in toto</u> analysis is no longer present. However, the day-to-day variation in tapes is significant.

It is apparent from the two reproducibility studies which have been finished that a tester variation will indeed remain a significant source of error. The differences between tapes prepared on separate days, although still a significant source of error, can be eliminated by preparing all tapes for response at one level of carbon dioxide on the same day. All other significant sources of error appear to have been eliminated, and it is felt that approximately a ±10 second deviation from the response mean can be obtained.

6.2 Environmental Influence on Tape Response Time

To estimate the effect of the three contractually specified environmental conditions -- temperature, pressure, and relative humidity -- on each other, a $(3)^3$ full factorial design was utilized. A full factorial design involves every combination of the levels of the factors being studied. The base figure in the $(3)^3$ figure indicates the number of levels being studied, while the exponential figure indicates the number of factors being studied. Table 23 shows the factors and levels which were studied.

Each experimental condition was replicated twice, giving a total of 54 experiments. The responses used for the analysis were the results after 2 hours under the stated conditions. One person made all the tests, thus eliminating tester variation.

An analysis of the experimental design indicates the shape of the response curve for each of the three factors. Because three levels are being studied, the linear component, or slope, and the quadratic component, or curvature, can be determined through the use of the following equations:

$$\text{Slope} = (-Y_0 + 0 + Y_2)/2$$

$$\text{Curvature} = (Y_0 - 2Y_1 + Y_2)/2$$

The Y's correspond to the response at the low (0), middle (1), and high (2) levels of the factor.

The interactions between the linear and quadratic components of each factor can also be determined; i.e., an interaction between the linear effect of temperature and the linear effect of pressure would indicate differences between the slopes of the temperature response lines for each

TABLE 23

EXPERIMENTAL CONDITIONS FOR
ENVIRONMENTAL TESTS

Levels of Temperature (0°F)	Levels of Pressure (psia)								
	3			13.25			23.5		
	Levels of Relative Humidity (%)								
	15	57.5	100	15	57.5	100	15	57.5	100
40									
80									
120									

level of pressure. The effects that can be determined from this $(3)^3$ full factorial design are as follows:

Main effects

- Temperature
  - Linear
  - Quadratic
- Pressure
  - Linear
  - Quadratic
- Relative Humidity
  - Linear
  - Quadratic

Two-Factor Interactions

- Temperature x Pressure
  - Linear T x Linear P
  - Linear T x Quadratic P
  - Quadratic T x Linear P
  - Quadratic T x Quadratic P
- Temperature x Relative Humidity
  - Linear T x Linear r.h.
  - Linear T x Quadratic r.h.
  - Quadratic T x Linear r.h.
  - Quadratic T x Quadratic r.h.

Relative Humidity x Pressure

Linear r.h. x Linear P

Linear r.h. x Quadratic P

Quadratic r.h. x Linear P

Quadratic r.h. x Quadratic P

Three-Factor Interactions

Temperature x Pressure x Relative Humidity

The difference between replicates of the experimental responses affords an estimate of experimental error. An "F" test was used to determine the significance of any main effect or interaction. The "F" test is the ratio of the variance for the effect being estimated to that of the experimental error. An effect is judged to be significant if the tabulated "F" value exceeds that specified in an "F" table. "F" test tables are available in most statistics books.

A full factorial design was used so that all significant interactions could be determined. It was felt that if one or more of the factors being studied does not interact with the other factors, then future experiments could be made by utilizing a fractional factorial design.

Fractional factorial designs employ the principle of confounding. Confounding involves setting an interaction, which is known to have no effect, equal to a factor about which information is desired. Any significance then found for the interaction is due to the equaled factor. This method greatly reduces the number of experiments necessary for determining the significance of a group of factors.

As reported previously, a special device was used to open the badges in a sealed glove box. This glove box was charged with oxygen containing 4- or 6 mm partial pressures of CO_2.

To set the levels of CO_2 in the glove box after installing the badges in the opener, the following procedure was used. The box was evacuated with a vacuum pump to a 2-mm vacuum or better. At the same time a glass bulb provided with two stopcocks was evacuated to a 1-mm vacuum. From a CO_2 tank, which was connected to one end of the above-mentioned bulb, the necessary amount of CO_2 was introduced into the bulb to obtain a 4- or 6-mm partial pressure of CO_2 in the glove box. The bulb used in the laboratory had a volume of 1109 ml and was filled with CO_2 to a pressure of 316 mm of mercury. When this amount of CO_2 was transferred into the box, the partial pressure of CO_2 in the box was 4 mm of mercury. For the level of a 6-mm partial pressure of CO_2, the bulb was filled with CO_2 to a pressure of 473 mm of mercury.

After filling the CO_2 bulb with the appropriate amount of CO_2, one end of the bulb was connected to a stopcock on the glove box and the other end was connected to an oxygen cylinder. Then all the stopcocks were opened, and oxygen was introduced into the evacuated glove box through the bulb until the pressure reached 3 psia. After the humidity and temperature equilibrated at the desired level, the tapes were opened and their response times recorded.

The same procedure was used to obtain the results at 13.25 and 23.5 psia. When the condition to which the box is set is 0% r.h., the oxygen used to obtain the different pressures was passed through an active molecular sieve column. Using this technique, the 0% r.h. was obtained faster in the glove box. Similarly, a condition with 100% r.h. was reached faster when the oxygen was introduced across a gas wash bottle containing distilled water. The results obtained and the statistical studies made are given in tables 24, 25, and 26.

The responses to the given experimental conditions were placed in standard order,* and a simple extension of Yates' analysis for 2^n factorial designs was used for the analysis. The actual calculations are shown in table 24. A summary of the statistical analysis and an estimate of the experimental error are found in table 25. The experimental error was obtained from the duplicate responses of the 27 tests.

Based on the results of the analysis, it is concluded that, under the testing conditions, none of the factors studied have any significant effect on the tape response time.

6.3 Storage Stability of Chemical Tapes

6.3.1 Storage at Room Temperature

To ascertain the long-range stability of the detection tapes, a quantity of them were stored for 90 days at room temperature. A random selection of them was made periodically, and these were tested at the levels of CO_2 for which they were designed. The response times obtained were plotted against storage times. These plots are shown in figures 14 through 22. It is seen that considerable variation occurred during the first week in all cases, but that the tapes yield far more reproducible responses in the ensuing periods. The average of two responses was taken

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* Davies, Design and Analysis of Industrial Experiments, p. 366, 2nd Edition, Hofner (1960).

TABLE 24

EXPERIMENTAL CONDITIONS (DESIGN AND RESULTS)

Variables	Levels 0	Levels 1	Levels 2
Temperature (°F)	40	80	120
Pressure (psia)	3	13-1/4	23-1/2
Relative Humidity(%)	0	50	100

Experiment Number	Temperature	Pressure	Relative Humidity	Result (Seconds*)
1	0	0	0	36.0
2	1	0	0	31.0
3	2	0	0	34.5
4	0	1	0	35.5
5	1	1	0	29.5
6	2	1	0	38.5
7	0	2	0	36.0
8	1	2	0	36.0
9	2	2	0	34.0
10	0	0	1	36.0
11	1	0	1	33.5
12	2	0	1	33.5
13	0	1	1	36.5
14	1	1	1	34.0
15	2	1	1	35.5
16	0	2	1	36.5
17	1	2	1	32.0
18	2	2	1	39.5
19	0	0	2	37.5
20	1	0	2	32.0
21	2	0	2	35.5
22	0	1	2	34.0
23	1	1	2	40.0
24	2	1	2	35.5
25	0	2	2	38.5
26	1	2	2	38.5
27	2	2	2	36.5

*Average of two responses

TABLE 25

ANALYSIS CALCULATIONS

Treatment* Combinations	Response (Seconds)	(1)	(2)	(3)	(4)	Mean Square
$t_oP_oR_o$	36.0	101.5	311.0	956.0		
$t_1P_oR_o$	31.0	103.5	317.0	-3.5	18	0.68
$t_2P_oR_o$	34.5	106.0	328.0	36.5	54	24.67
$t_oP_1R_o$	35.5	103.0	-0.5	18.0	18	18.00
$t_1P_1R_o$	29.5	106.0	-0.5	5.0	12	2.08
$t_2P_1R_o$	38.5	108.0	-2.5	-12.0	36	4.00
$t_oP_2R_o$	36.0	105.0	21.5	-1.0	54	0.02
$t_1P_2R_o$	36.0	109.5	18.5	-14.0	36	5.44
$t_2P_2R_o$	34.0	113.5	-3.5	11.0	108	1.12
$t_oP_oR_1$	36.0	-1.5	4.5	17.0	18	16.05
$t_1P_oR_1$	33.5	3.0	5.0	-2.0	12	0.33
$t_2P_oR_1$	33.5	-2.0	8.5	-25.0	36	17.36
$t_oP_1R_1$	36.5	-2.5	-0.5	4.0	12	1.33
$t_1P_1R_1$	34.0	-1.0	5.5	0.5	8	0.03
$t_2P_1R_1$	35.5	3.0	0.0	-0.5	24	0.01
$t_oP_2R_1$	36.5	-2.0	-10.5	-1.0	36	0.03
$t_1P_2R_1$	32.0	1.5	9.5	2.5	24	0.26
$t_2P_2R_1$	39.5	-2.0	-11.0	51.5	72	36.84
$t_oP_oR_2$	37.5	8.5	0.5	5.0	54	0.46
$t_1P_oR_2$	32.0	15.0	-1.0	-2.0	36	0.11
$t_2P_oR_2$	35.5	-2.0	-0.5	-19.0	108	3.34

TABLE 25 (Continued)

Treatment* Combinations	Response (Seconds)	(1)	(2)	(3)	(4)	Mean Square
$t_oP_1R_2$	34.0	2.5	-9.5	3.0	36	0.25
$t_1P_1R_2$	40.0	4.0	2.5	-11.5	24	5.51
$t_2P_1R_2$	35.5	12.0	-7.0	-40.5	72	22.78
$t_oP_2R_2$	38.5	9.0	-23.5	2.0	108	0.04
$t_1P_2R_2$	38.5	-10.5	6.5	-21.5	72	6.42
$t_2P_2R_2$	36.5	-2.0	28.0	-8.5	216	0.33

*Subscript of letters (t = temperature, P = pressure, R = relative humidity) indicate level used in the experiment.

TABLE 26

COMPLETE ANALYSIS OF VARIANCE OF TABLE 24

Source of Variation		Mean Square	Variance of Ratio*
Main Effects:			
Temperature	Linear	0.68	0.06
	Quadratic	24.67	2.08
Pressure	Linear	18.00	1.52
	Quadratic	0.02	0.001
Relative humidity	Linear	16.05	1.35
	Quadratic	0.46	0.04
Two-Factor Interactions:			
Linear temperature-linear pressure		2.08	0.18
Quadratic temperature-linear pressure		4.00	0.34
Linear temperature-quadratic pressure		5.44	0.46
Quadratic temperature-quadratic pressure		1.12	0.10
Linear temperature-linear relative humidity		0.35	0.03
Quadratic temperature-linear relative humidity		17.36	1.46
Linear temperature-quadratic relative humidity		0.11	0.01
Quadratic temperature-quadratic relative humidity		3.34	0.28
Linear pressure-linear relative humidity		1.33	0.11
Quadratic pressure-linear relative humidity		0.03	0.00
Linear pressure-quadratic relative humidity		0.25	0.02
Quadratic pressure-quadratic relative humidity		0.04	0.00
Three-factor interactions:		9.02	0.76

Estimate of experimental error based on differences between responses of tapes run under identical environmental conditions.

$S^2 = 11.85$ Standard deviation $S = 3.44$

Based on appropriate statistical test comparing variances, a value of the variance ratio ≥ 4.21 is necessary for factor significance. Therefore, under the testing conditions, the effect on response time of the factors studied is insignificant.

*Ratio of mean square: S^2.

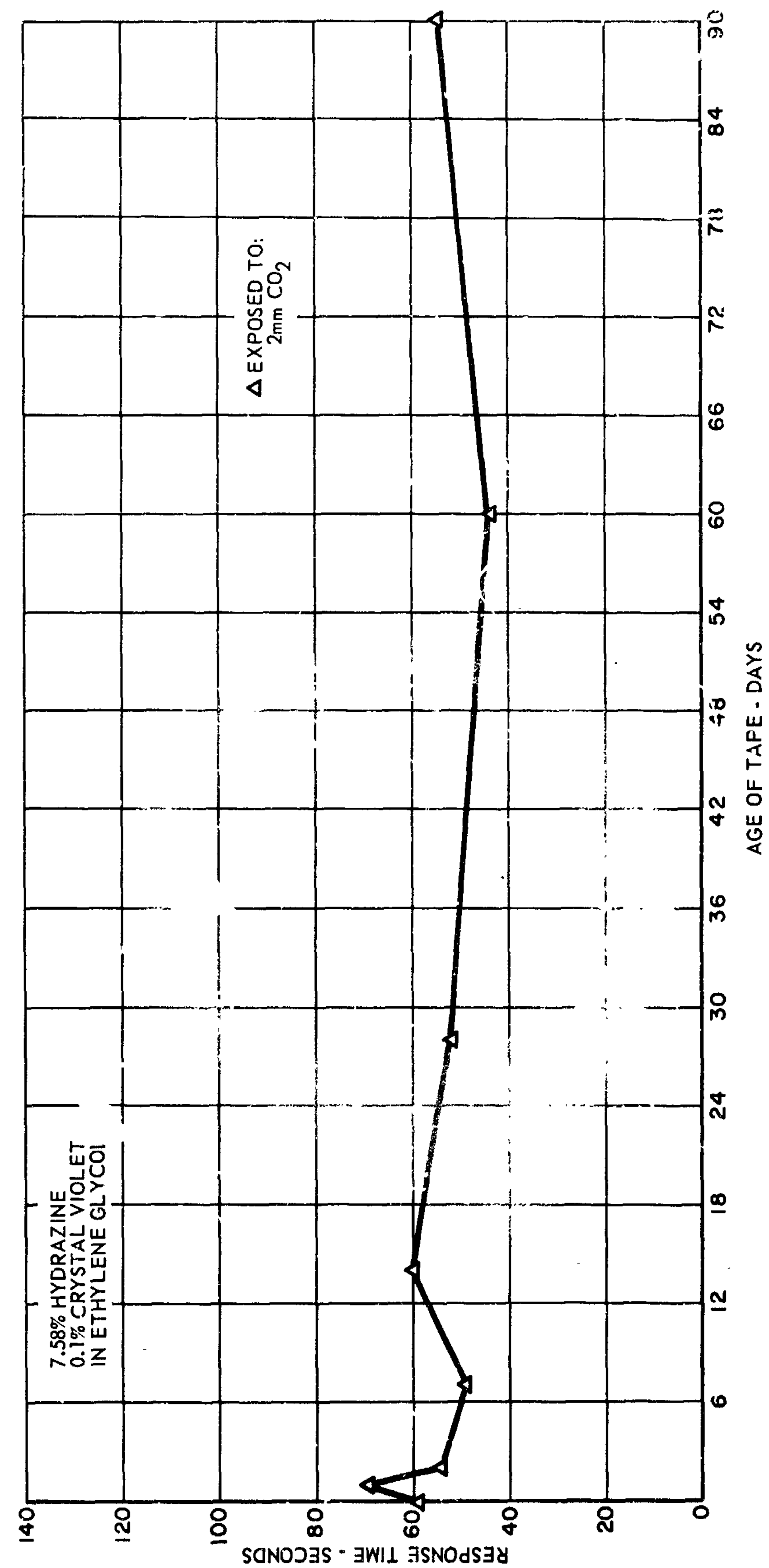

Figure 14. Storage Test Results on Crystal Violet-Hydrazine Tapes (7.58% Hydrazine)

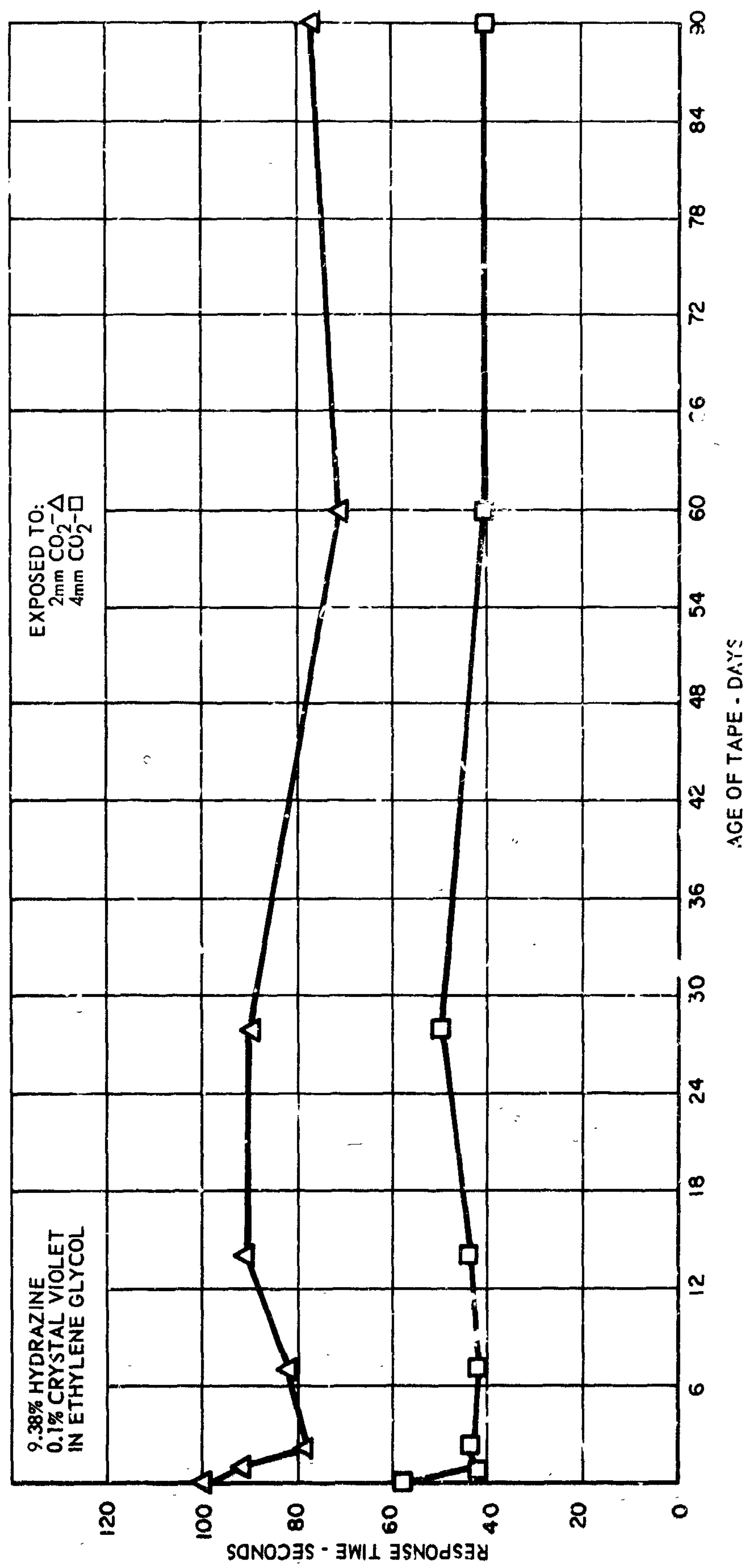

Figure 15. Storage Test Results on Crystal Violet-Hydrazine Tapes (9.38% Hydrazine)

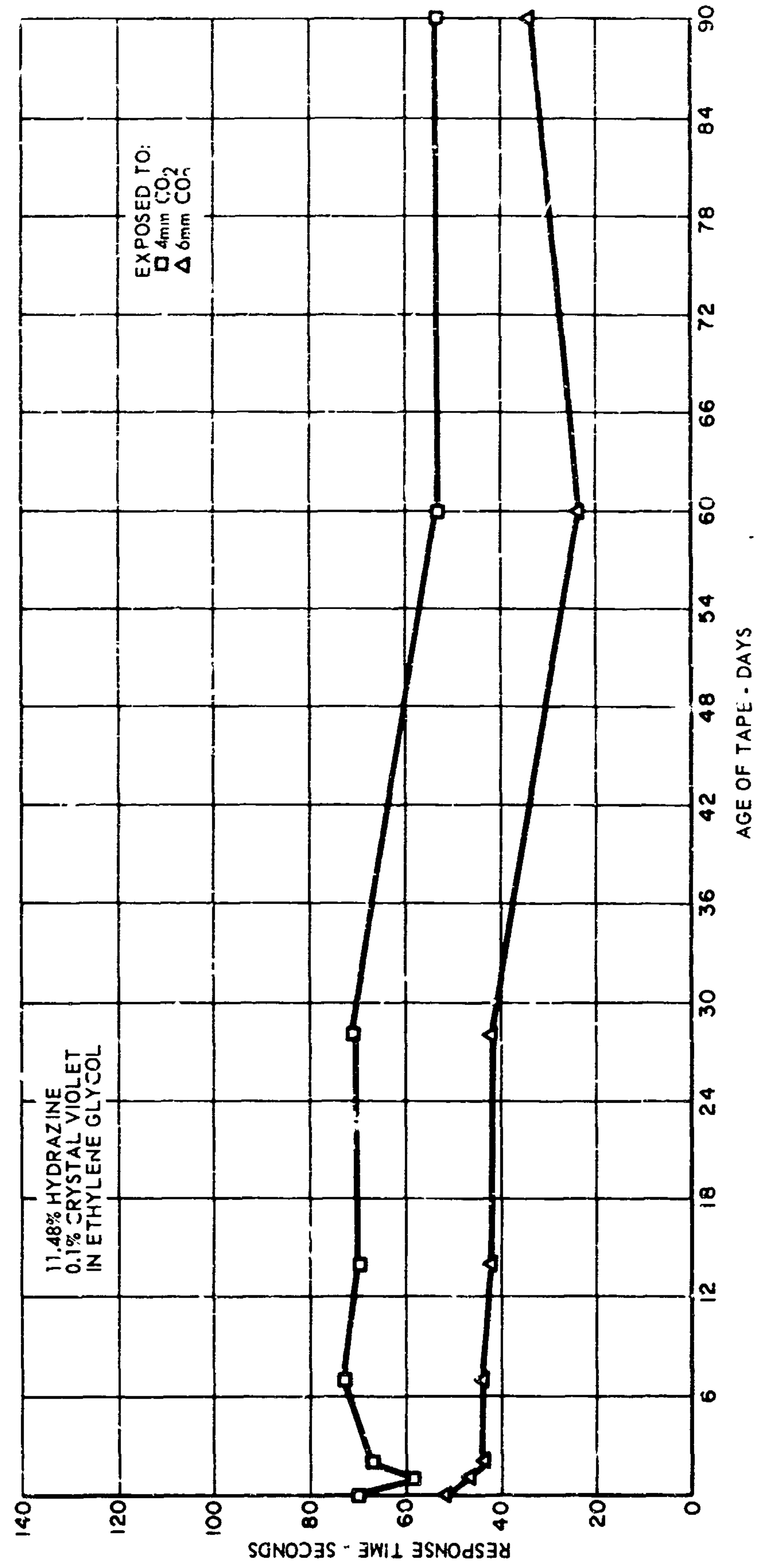

Figure 16. Storage Test Results on Crystal Violet-Hydrazine Tapes (11.48% Hydrazine)

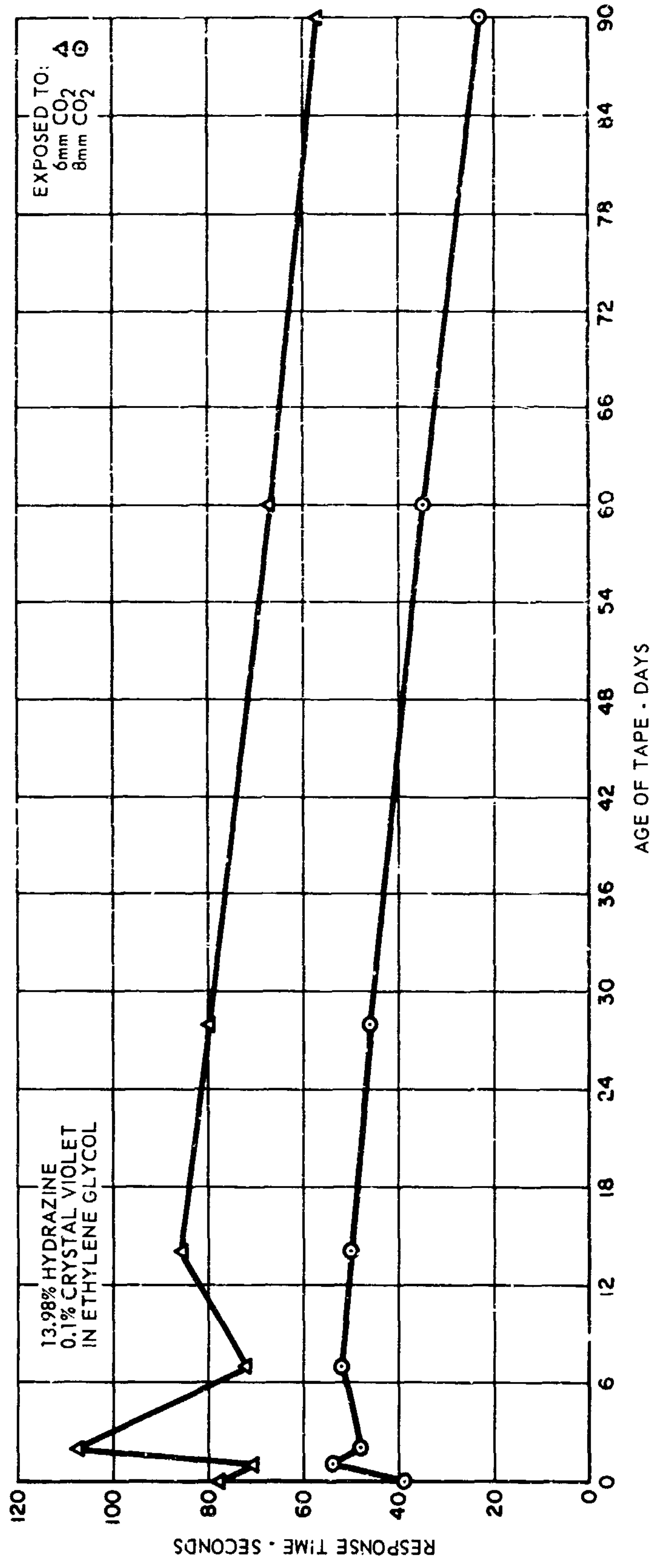

Figure 17. Storage Test Results on Crystal Violet-Hydrazine Tapes (13.98% Hydrazine)

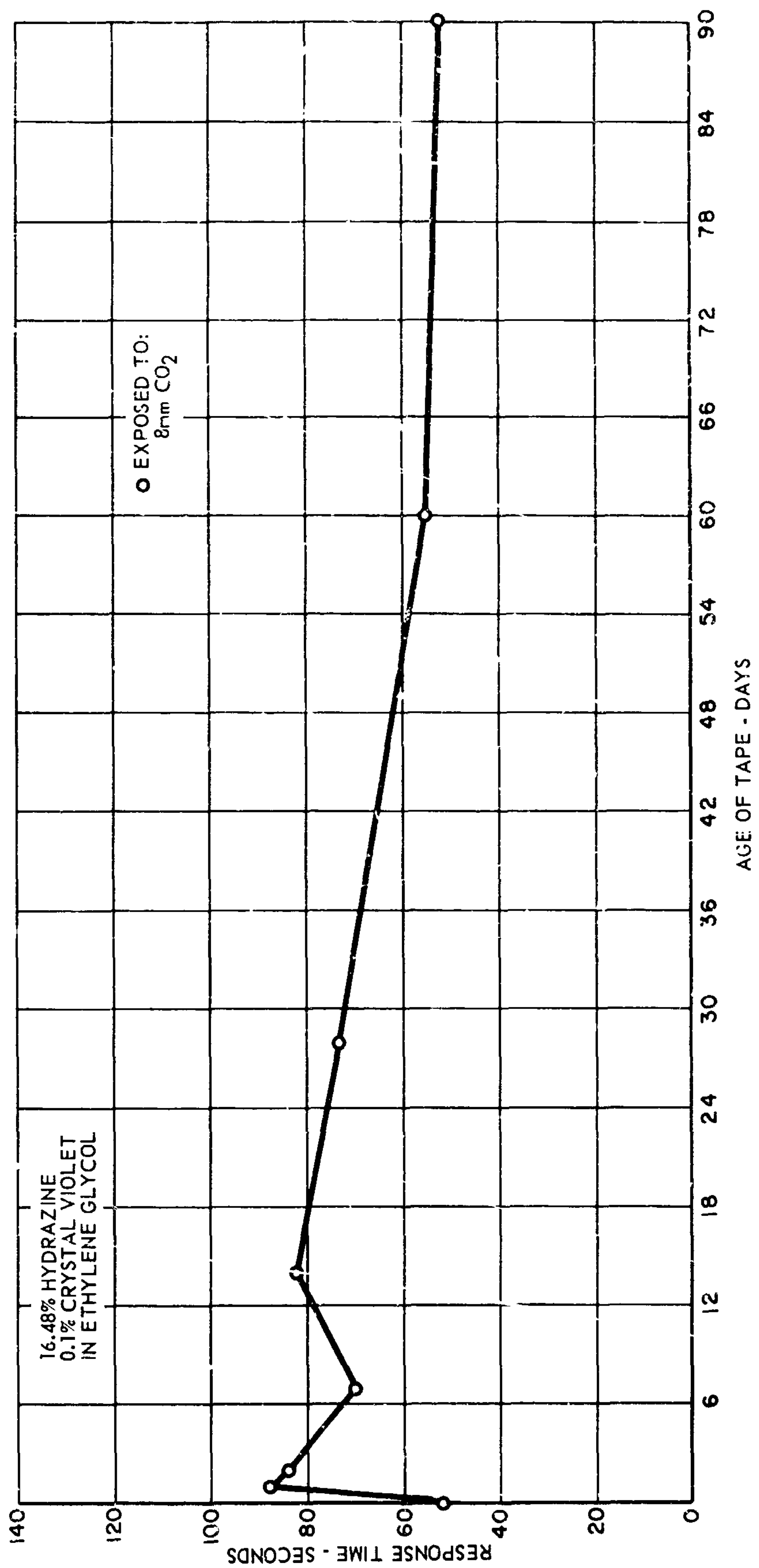

Figure 18. Storage Test Results on Crystal Violet-Hydrazine Tapes (16.48% Hydrazine)

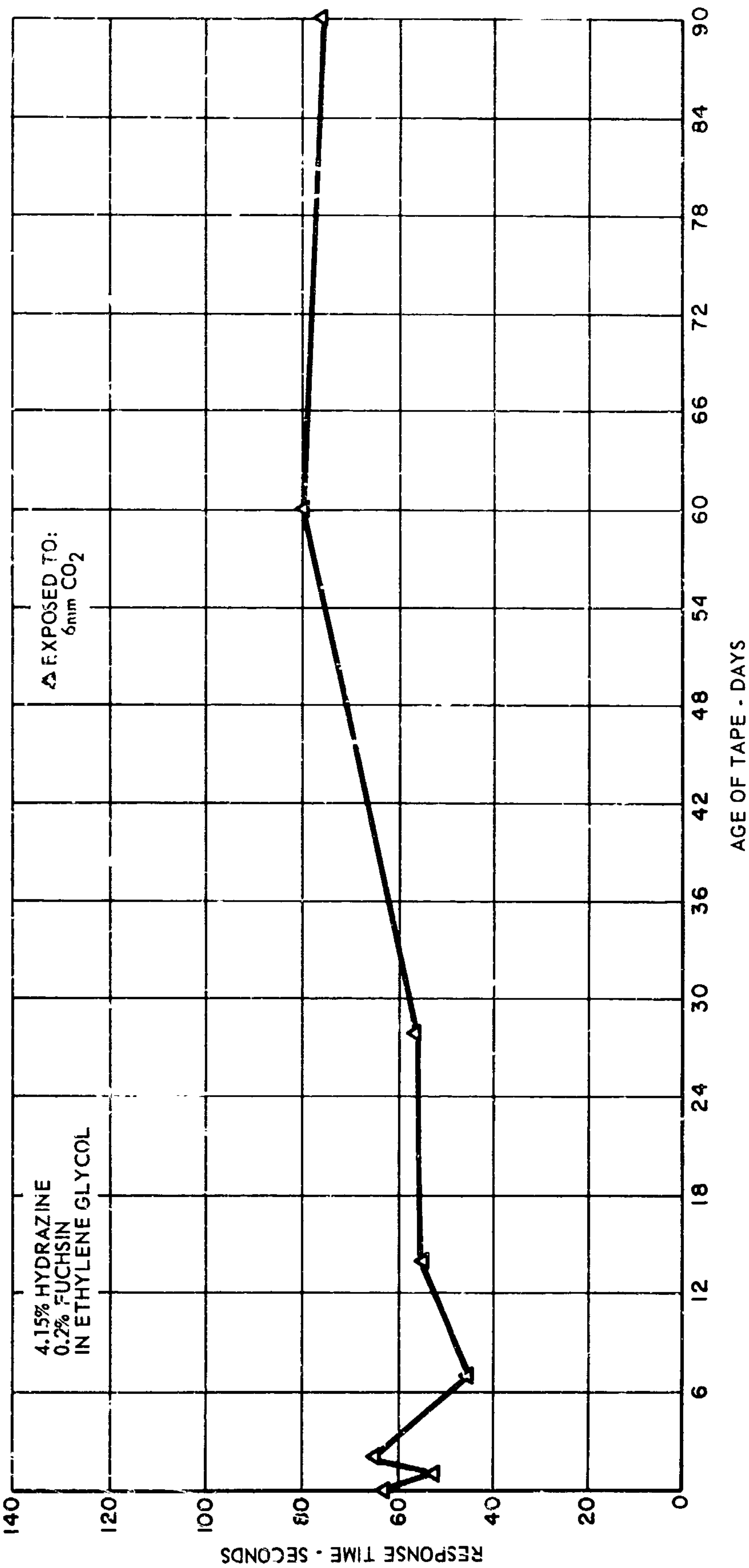

Figure 19. Storage Test Results on Basic Fuchsin-Hydrazine Tapes (4.15% Hydrazine)

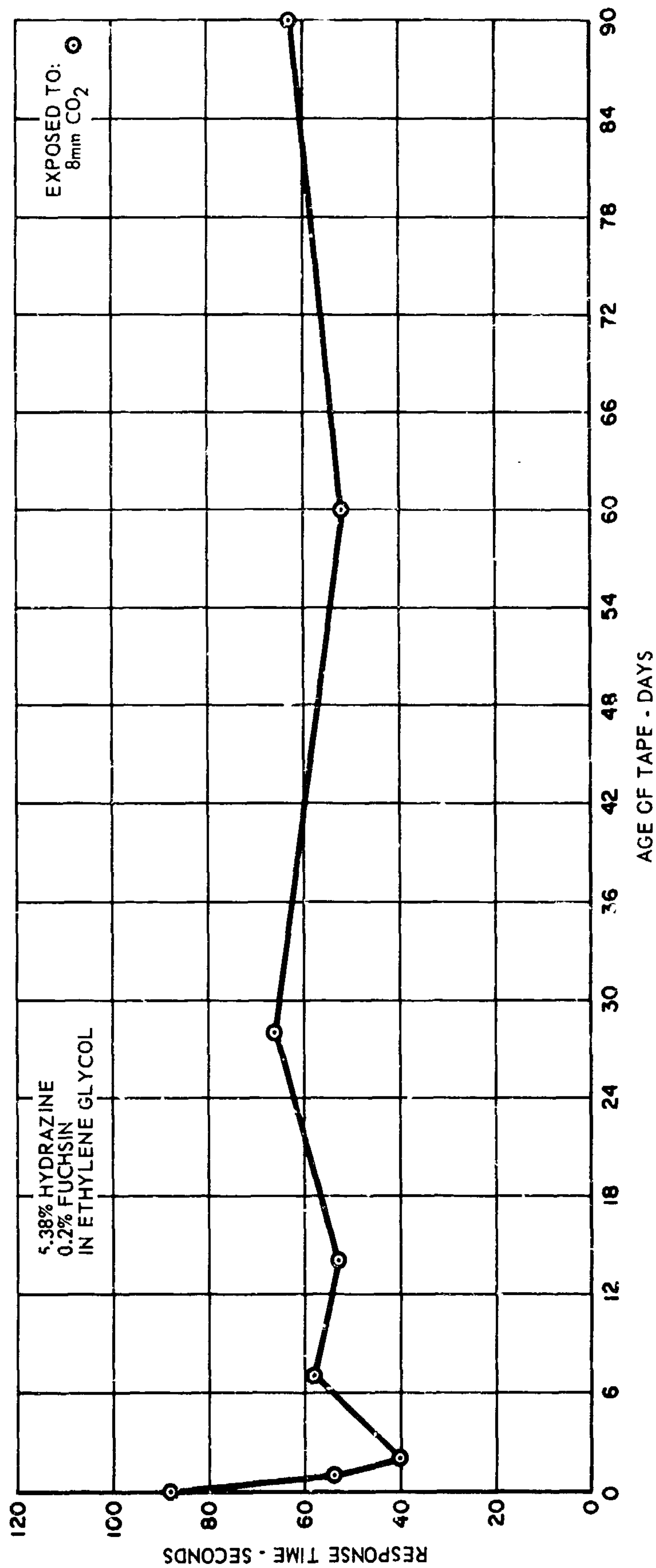

Figure 20. Storage Test Results on Basic Fuchsin-Hydrazine Tapes (5.38% Hydrazine)

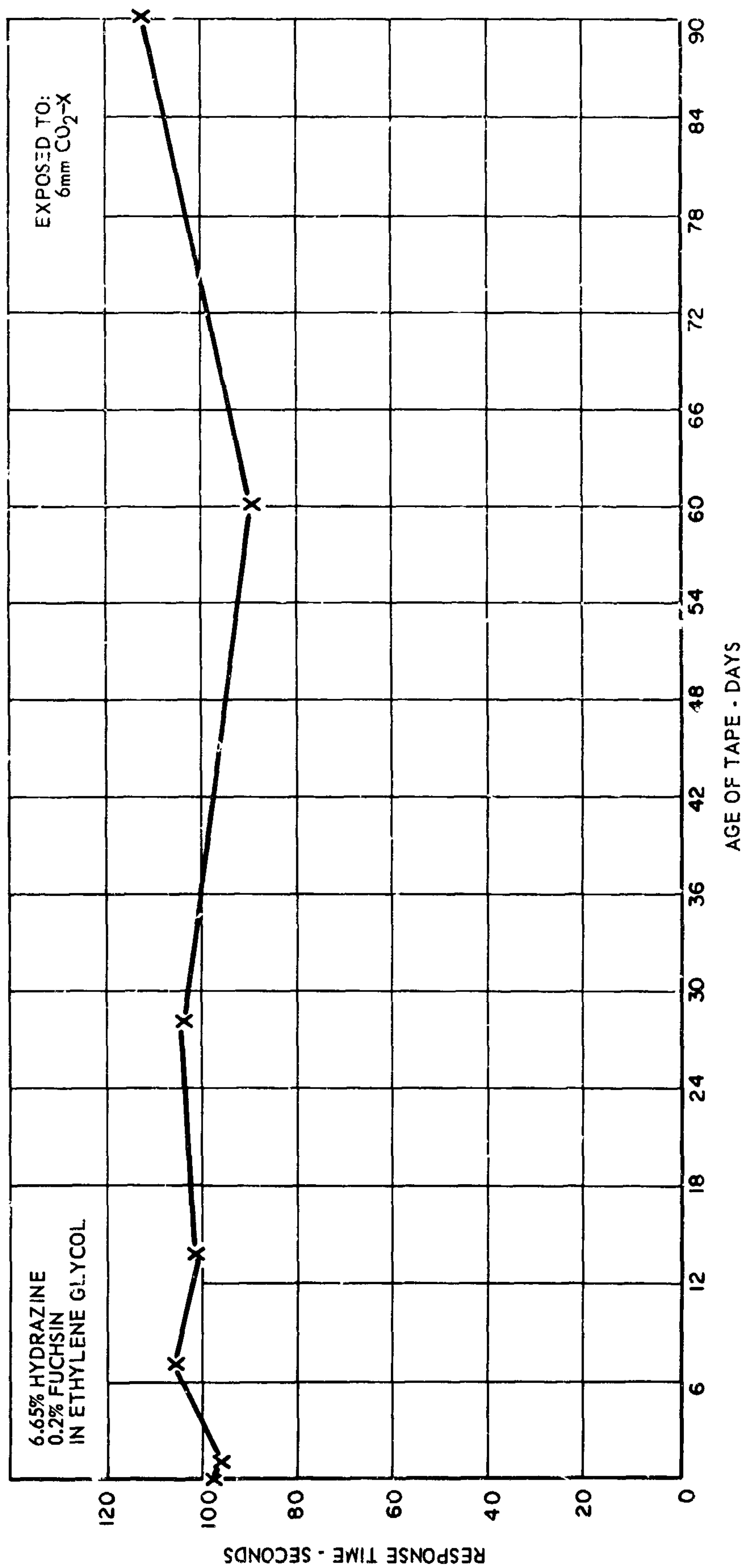

Figure 21. Storage Test Results on Basic Fuchsin-Hydrazine Tapes (6.65% Hydrazine)

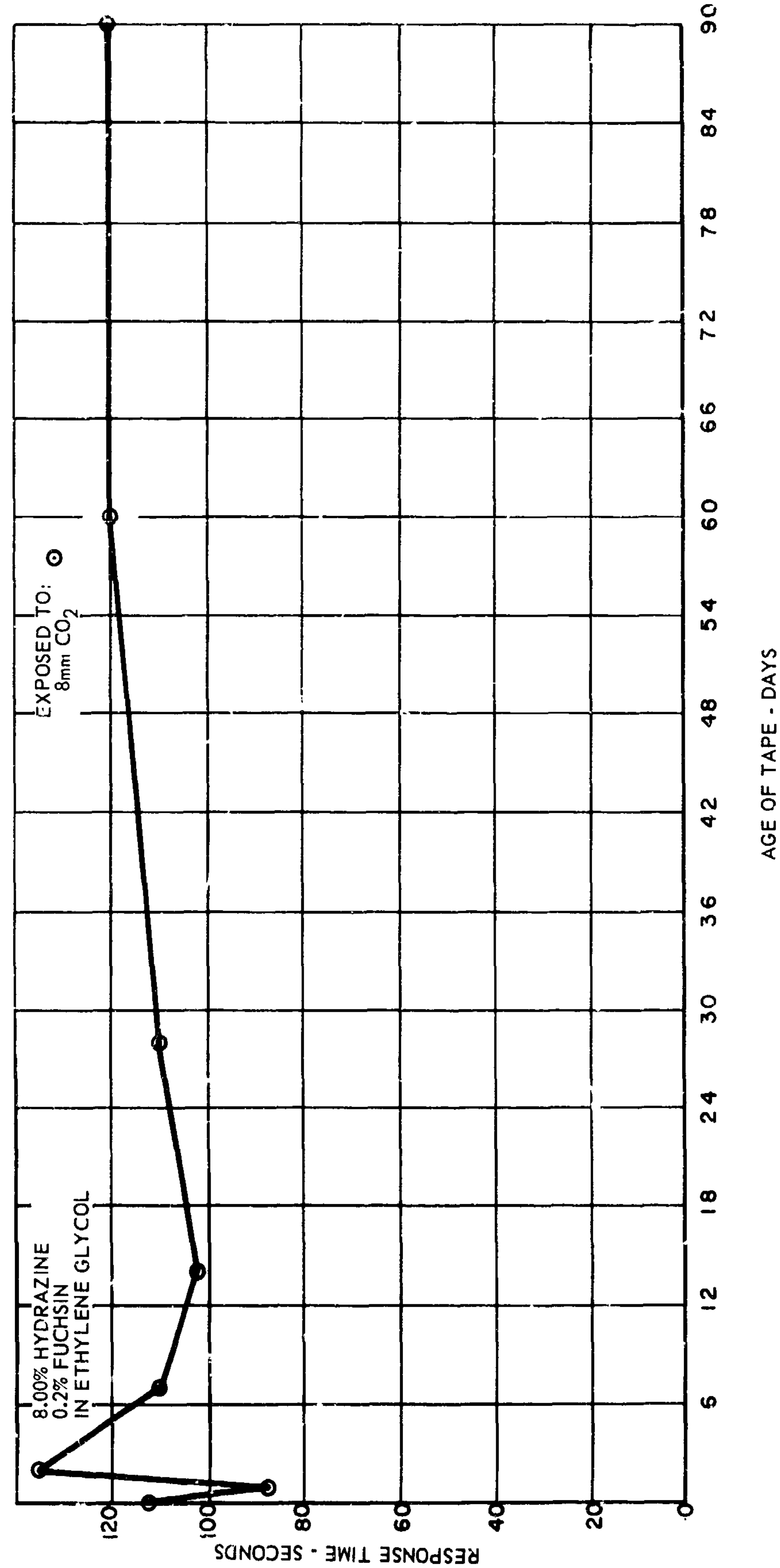

Figure 22. Storage Test Results on Basic Fuchsin-Hydrazine Tapes (8.00% Hydrazine)

for each point plotted on the graph; and in each case, the initial point was determined from a freshly prepared tape.

It should be noted that several different concentrations of hydrazine were used during the study, with both the Crystal Violet and the Basic Fuchsin dyes, to examine the behavior of the tapes during this extended period. All tended to stabilize quite well, although the response times of some of these tapes were not within the desired limits.

6.3.2 Storage at Elevated Temperature

A series of storage stability tests were made on reactive tapes individually packed in aluminized Mylar bags and stored in ovens at temperatures of 90°, 100°, 110°, 130°, and 160°F. The tapes were removed at periodic intervals and opened at known CO_2 concentrations. As shown in figures 23 and 24, some widely variant results were obtained. In figure 23, the tape kept at 90°F remained fairly stable during the testing period; the tape stored at 100°F remained stable up to the 329-hour point, then increased rapidly in response time; and the tape stored at 110°F diverged greatly after 140 hours.

In figure 24, it is seen that the tape stored at 130°F begins to vary after 24 hours; while, as would be expected, the tape stored at 160°F diverges more rapidly, the change being first noted after 6 hours.

It should be noted here that current investigations utilizing tetraethylenepentamine instead of hydrazine as the basic reducing agent show that a far greater measure of stability with respect to elevated temperatures can be achieved.

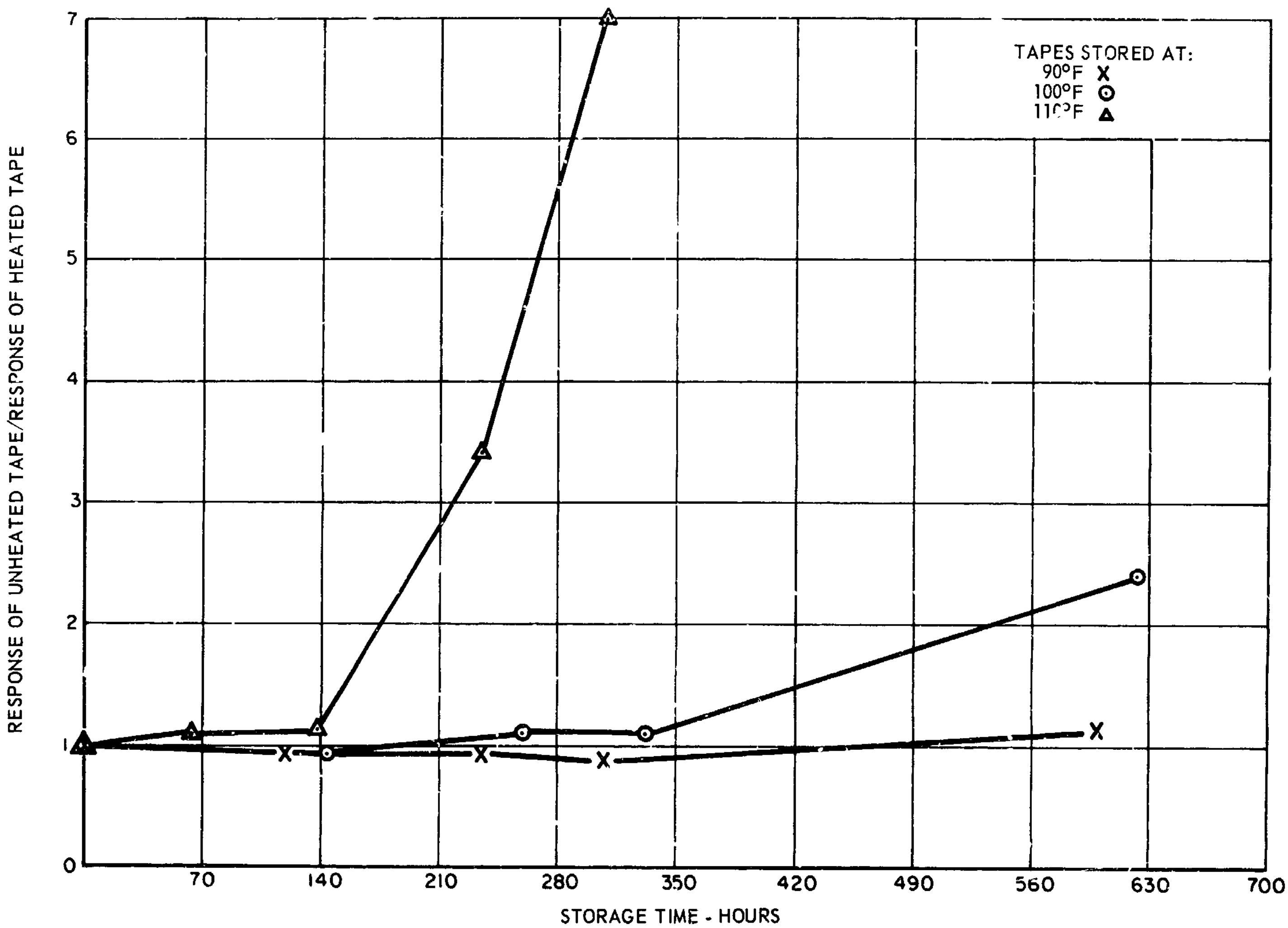

Figure 23. Storage Time at 90°, 100°, and 110°F Versus Change in Response Time

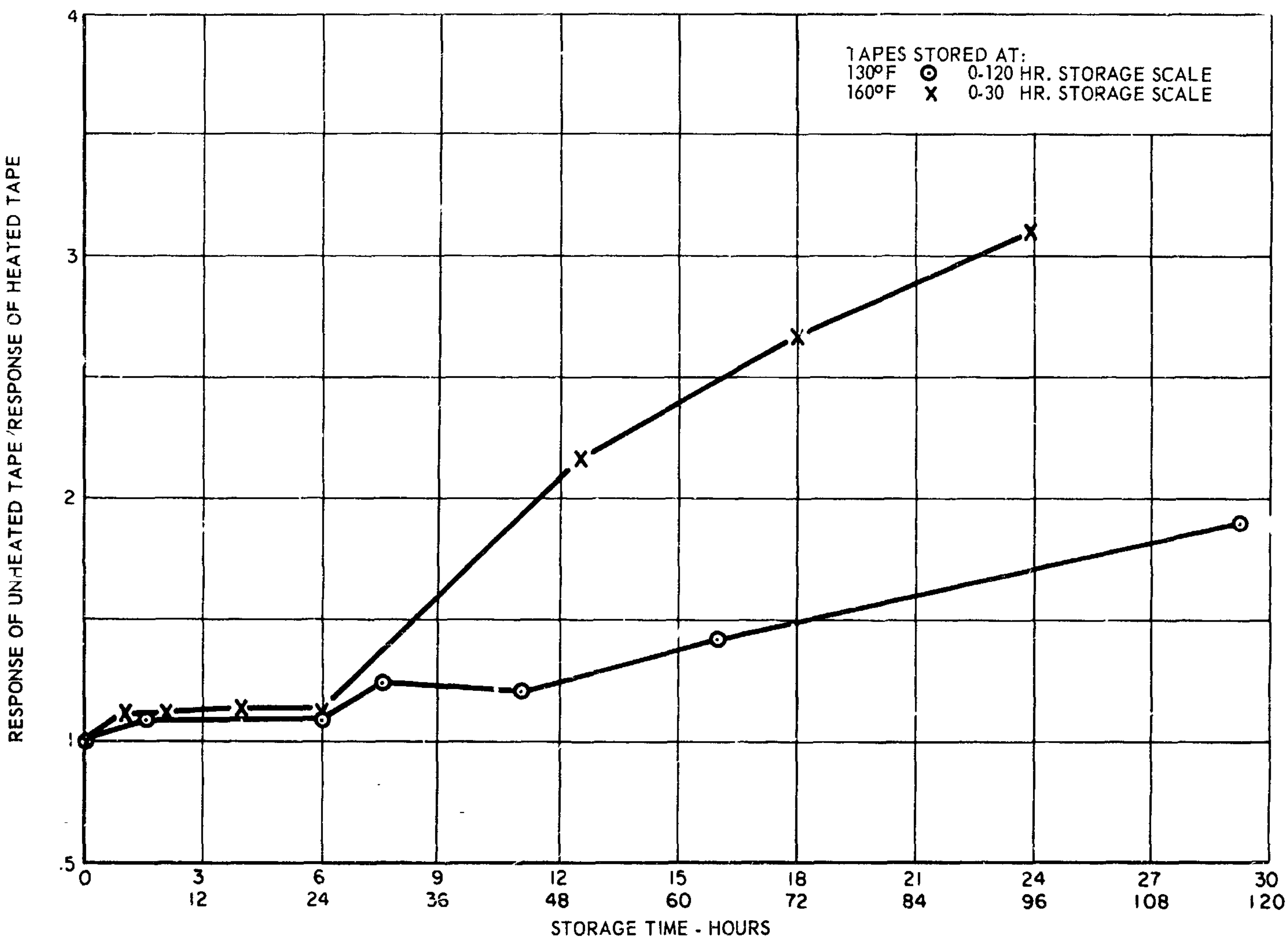

Figure 24. Storage Time at 130° and 160°F Versus Change in Response Time

6.3.3 Storage Over 3-Month Period

Table 27 gives the response times of tapes stored from 1 day to 3 months in various conditions of temperature and humidity. The tests are carried out at atmospheric pressure. The 8-mm tapes used in these storage tests were slightly slower than the 35±6 second response. The tapes were stored in badges, and the badges were cut into four parts and each level tested separately. The badges used in the storage tests were not the improved design and, therefore, could be the cause of some of the out-of-limit response times. The 2-mm tape was tested at a 2-mm partial pressure of CO_2, the 4-mm tape at a 4-mm partial pressure of CO_2, etc.

As is seen from table 27, the only tapes that withstood the 3-month storage were those stored at 20°F and 0% r.h. The tapes stored at 75°F (0% r.h. and 100% r.h.) gave good responses up to 1 month's storage. The tapes stored at 90°F (0% r.h. and 100% r.h.) were either out of limits or bad after 1 month's storage.

TABLE 2

STORAGE STABILIT

Response Time i

Storage Time	20°F, 0% r.h. 2mm	4mm	6mm	8mm	75°F, 0% r.h. 2mm	4mm	6mm	8mm	75 2mm
1 day	32	33	31	37	36	32	35	41	34
2 days	35	38	34	38	32	38	34	37	37
1 week	33	39	41	35	38	38	42	42	35
2 weeks	32	35	38	46	34	33	38	43	40
1 month	32	32	39	37	32	35	39	39	29
2 months	34	40	34	31	30	26	26	25	38
3 months	31	31	36	39	30	17	39	30	26

91-1

7

Y OF TAPES

n Seconds

°F, 100% r.h.				90°F, 0% r.h.				90°F, 100% r.h.		
4mm	6mm	8mm	2mm	4mm	6mm	8mm	2mm	4mm	6mm	8mm
37	37	47	33	34	35	43	33	36	35	45
41	36	36	39	33	38	42	35	36	37	46
34	40	36	38	41	40	35	39	39	39	37
30	34	40	36	36	41	38	37	38	37	33
31	30	37	21	19	34	41	52	Bad	24	35
Bad	23	32	33	22	31	23	Bad	Bad	36	49
16	37	43	5	5	27	13	Bad	Bad	36	78

7. HYDRAZINE EVOLUTION FROM CARBON DIOXIDE DETECTOR TAPES

It was early recognized that hydrazine might possibly be objectionable because of its known toxicity, which is reported to be 1 ppm for an 8-hour period. (Recent toxicity data collected on dogs show this level to be 5 ppm.*) However, the calculations that were made in connection with hydrazine evolution indicated that the amount of hydrazine to be found in the atmosphere at any one time would be well below this level; and the calculations indicated that the hydrazine concentration at any one time would be at most a few parts per billion within an atmosphere volume of 80 cubic feet and 5 psia of oxygen. The purpose of the effort was to confirm, or possibly repudiate, the calculations made at an earlier stage in this program.

It is to be recognized at the onset that hydrazine is inherently an unstable material. Since it is such a strong reducing material, it is quite subject to oxidation to such products as water and nitrogen. Hydrazine is also known to be degraded quite easily by catalytic materials, particularly metallic materials.** Since hydrazine is a strong base, it reacts quite readily with acidic compounds such as carbon dioxide to give salts. Most of the information related to the behavior of hydrazine has been derived from its reactions in the liquid form -- or at best, in solutions. Very little information is available for the vapor phase reactions

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* C. C. Comstock, et al., "Inhalation Toxicity of Hydrazine Vapor," <u>Arch. Ind. Hyg. Occupational Medicine</u>, Vol. 10 (1954).

** L. F. Andrieth and B. A. Ogg, <u>The Chemistry of Hydrazine</u>.

of hydrazine. The purpose of these investigations, then, was to confirm for gaseous hydrazine the instability data indicated by the solution and pure liquid data on hydrazine. The results of these investigations definitely show that, because of the instability characteristics of hydrazine under the environmental conditions to which it would be subjected, a toxicity problem associated with the release of hydrazine from the carbon dioxide detection badges is nonexistent.

7.1 Total Hydrazine Vapor Loss from the Detectors with Time

To determine the hydrazine loss from a detector under an oxygen atmosphere, a 500-ml filter flask was used. It was fitted with a stopper through which the flask could be evacuated or alternately charged with oxygen. The oxygen pressure in the flask was reduced to 5 psia. The opened badge was allowed to remain in this flask for 1 hour and was transferred to another flask, where it remained again for 1 hour (and so on until the end of the test). The hydrazine evolved from the badge was scrubbed from the air in the flask by pulling it through 2N HCl, and the walls of the flask were also washed with 2N HCl. The hydrazine in the combined 2N HCl is determined with a colorimetric reaction, using p-dimethylaminobenzaldehyde as the reagent.

Figure 25 gives the hydrazine evolution data obtained as described above. The ordinate gives the total amount of hydrazine evolved from the tape as a function of time. This total corresponds to the summation of the hydrazine released at hourly intervals. A correction in this plot has also been made for the effects of oxygen on the degradation of hydrazine

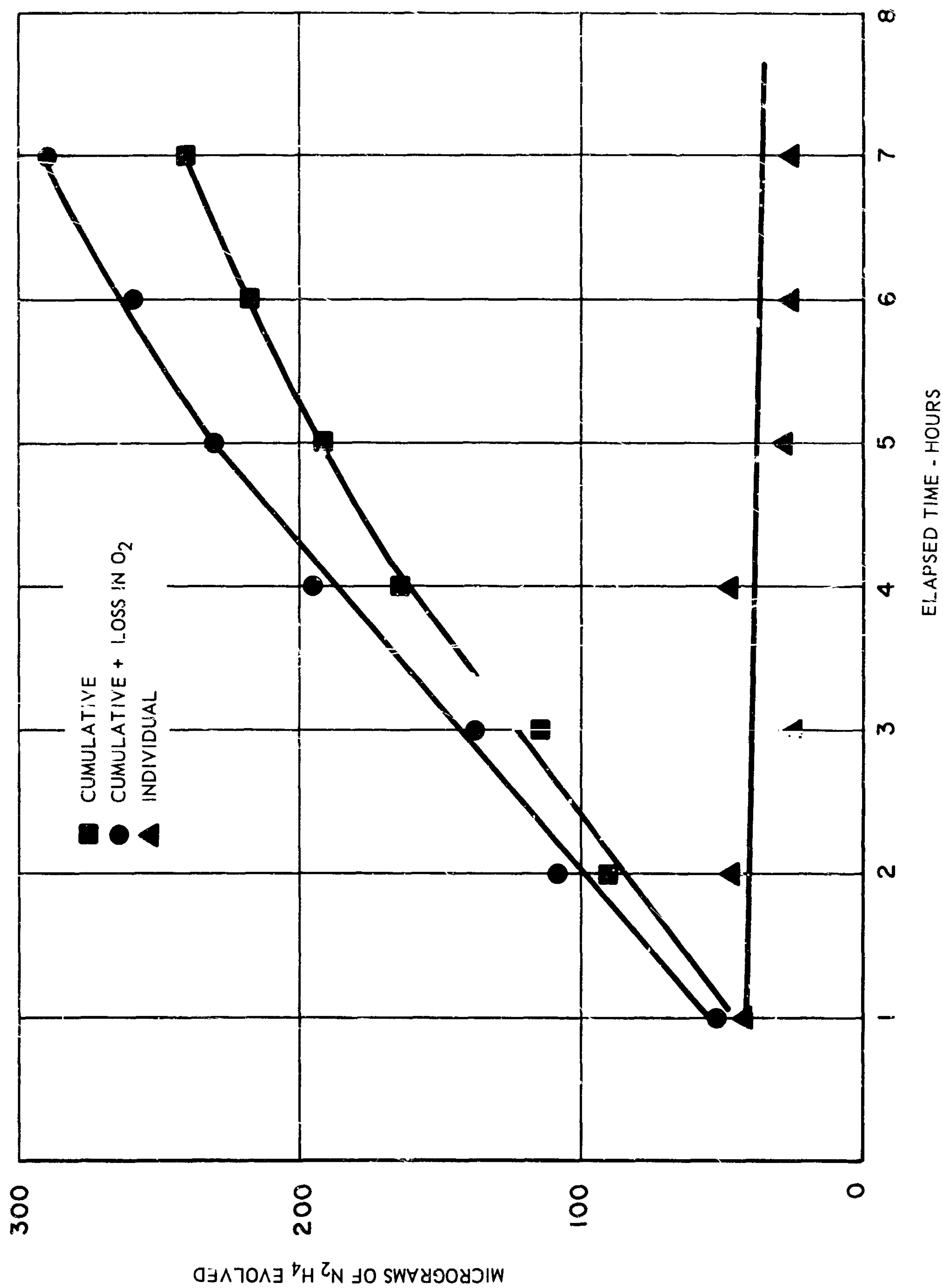


Figure 25. Hydrazine Evolution from CO_2 Detectors with Time

during the 1-hour period that it was exposed as a vapor. The release of hydrazine from the tape is also influenced to a certain extent by the reaction of liquid hydrazine within the tape with oxygen of the air. The effects of oxygen on the hydrazine, both in the vapor state and in the tape, will be covered in a subsequent paragraph. The plots in figure 25 represent hydrazine evolution essentially free of oxygen degradative reactions or any other degradative reactions.

The plots in figure 25 show that the evolution of hydrazine from the tapes is approximately exponential. The evolution data show that after a 7-hour exposure of the tape, there would be approximately 300 micrograms of hydrazine evolved. This would be equivalent to a concentration within the Gemini capsule (80 cubic feet, 5 psia) of approximately 0.3 ppm <u>if there were not losses of hydrazine by degradative reactions as it accumulates</u>. The nature of the degradative reactions after 7 hours indicates that significant accumulation of hydrazine from above the badge would not occur after this period of time.

7.2 Hyrdazine Accumulation Above the Badge in an Oxygen Atmosphere

The data of the previous section indicate the total hydrazine evolution from a badge into the atmosphere. The exposure times of hydrazine evolved were only 1 hour; and thus the full effects of the oxygen of the atmosphere on hydrazine degradation were not realized. The evolution of hydrazine as previously indicated was a measure of total hydrazine given off.

Since initial studies had shown that oxygen apparently did attack hydrazine in the gaseous state, it was of interest to determine just what the total hydrazine concentration was in air as a function of exposure time of a single badge at a 5-psia oxygen pressure.

The procedures and apparatus used were essentially those indicated in the previous paragraph. A 500-cc glass flask was filled with oxygen at atmospheric pressure, the badge was inserted and opened, and the oxygen pressure over the badge was not transferred from flask to flask. Instead, a given badge was left in the container for a prescribed period of time, after which it was removed and the total hydrazine content of the container was determined. A different badge was used for each exposure period.

It was found here (as in paragraph 7.1) that evolved hydrazine was strongly adsorbed to the side of the glass container, and that it was necessary to remove this adsorbed hydrazine by washing with 2N HCl in determining the total hydrazine evolved. Hydrazine adsorbed on the side of the container in many cases represented at least 75% of the total hydrazine evolved.

Data obtained on the evolution of hydrazine from the badges were somewhat scattered, and no definite trend in the data could be detected as a result of the scatter. The lack of a trend here was in contrast to the marked decrease in hydrazine vapor concentration with exposure to 5 psia of oxygen. (Refer to paragraph 7.5.)

A closer examination of the tapes used in these experiments indicated that the individual pockets in the badges in which they were contained varied quite appreciably in size. Since the dead volume above the individual tapes containing hydrazine determines the equilibrium absolute amounts above the tapes, it is no wonder that consistent results were not obtainable. In the light of the accumulated data, it was not considered worthwhile to spend the time and effort in circumventing this particular difficulty.

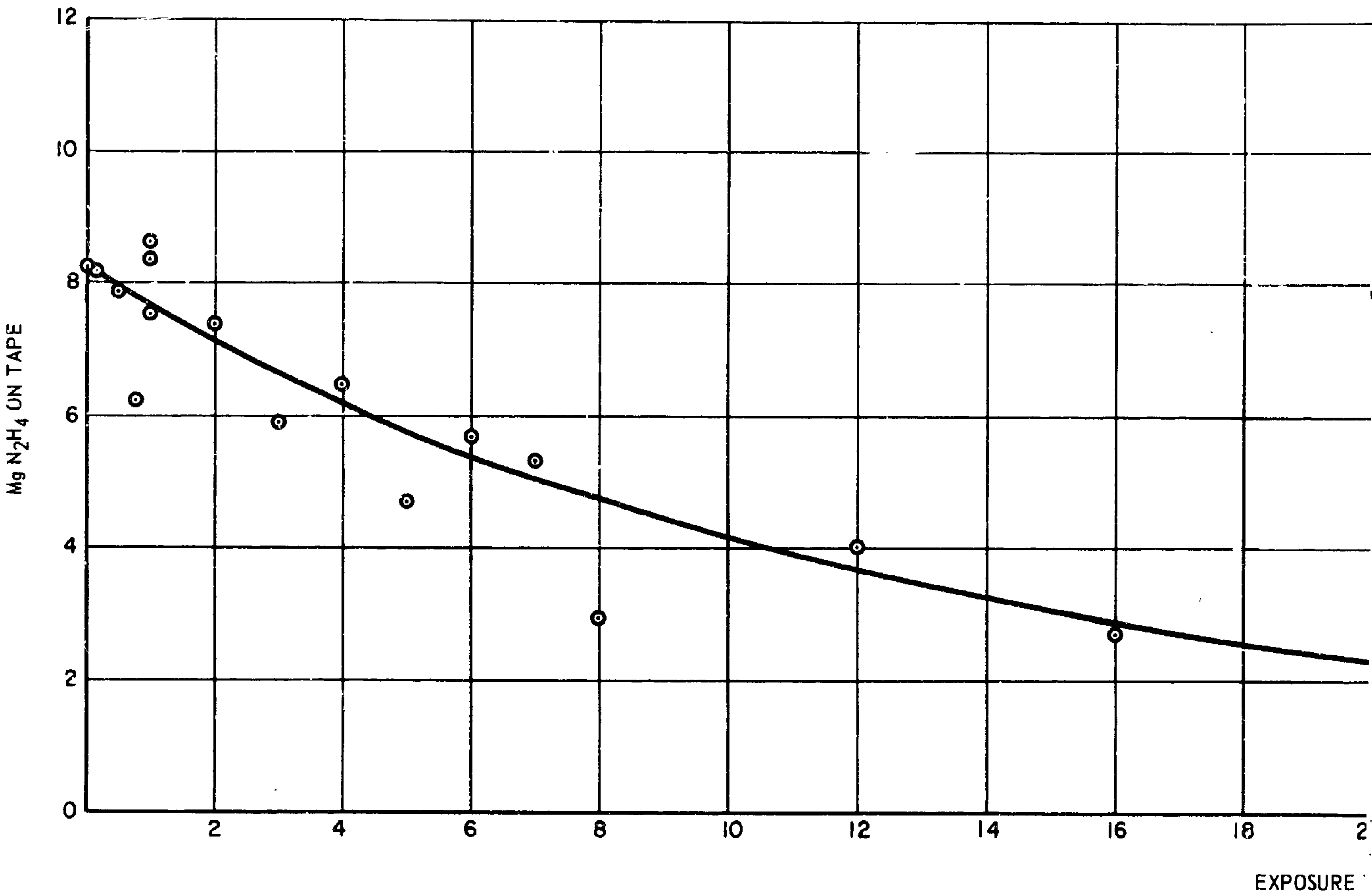
Some very significant conclusions were reached from the collected data even in the light of data scattering. Some 17 badges were exposed to 5 psia of oxygen for periods of time ranging from a few minutes up through 20 hours. The maximum amount of hydrazine released from any one badge was 150 micrograms, and this was realized after 1 hour. These 150 micrograms correspond to approximately 0.14 ppm within the Gemini capsule volume at 5 psia. A maximum of 50 micrograms of hydrazine was observed after some 20 hours. Note that this maximum quantity is in sharp contrast to the accumulated total of approximately 300 micrograms observed for the single badge. (See figure 25.) An effect of oxygen on released hydrazine as well as upon the residual liquid hydrazine in the individual tapes is indicated by this difference.

7.3 <u>Hydrazine Remaining on Tapes in the Detectors After Exposure to Oxygen</u>

In the light of the experimental difficulties in connection with the work carried out under paragraph 7.2, similar types of experiments were carried out in which the residual hydrazine left in the chemical tapes in the badges was measured. It was anticipated that since the amount of hydrazine vaporized from the tapes was relatively small as compared to the hydrazine present initially in the tapes, the problem of package volume associated with each tape would not be significant. Consequently, individual badges were opened and exposed in 5-psia atmospheres of oxygen for prescribed periods of time (as discussed in paragraph 7.2). At the end of the exposure periods the liquid hydrazine remaining in the tapes was determined by extracting them with a 2N HCl solution.

Figure 26 shows the milligrams of hydrazine remaining on all four tapes in the detection badge as a function of exposure time to oxygen at 5 psia. The slight dispersion of points here is attributable to the fact that all tapes do not contain initially the same absolute amount of hydrazine. The hydrazine and solution uptake by the filter papers is a function of the weight of the paper. No attempt was made to reproduce closely the weight of the filter paper test strips.

It is markedly evident from this plot that there is a very significant reduction in the residual liquid hydrazine content of the badge. This reduction leads to a lower rate of release of gaseous hydrazine to the atmosphere. From the data represented by figure 27, it is seen that the 8 milligrams initially present in the badge are reduced by a factor of 2 after 10 hours as a result of the reaction with oxygen. After 24 hours the hydrazine content is down to 2 milligrams, and after 40 hours to approximately 1 milligram. This decrease, as might be anticipated, is exponential. Since the rate of release of gaseous hydrazine should, at most, be proportional to the liquid hydrazine present in the badge, it would appear that after 24 hours this release rate is down to 25% of the initial rate. After 40 hours it is down to approximately 12%. It is anticipated that the release



Mg N_2H_4 ON TAPE
12
10
8
6
4
2
0
2
4
6
8
10
12
14
16
18
2
EXPOSURE

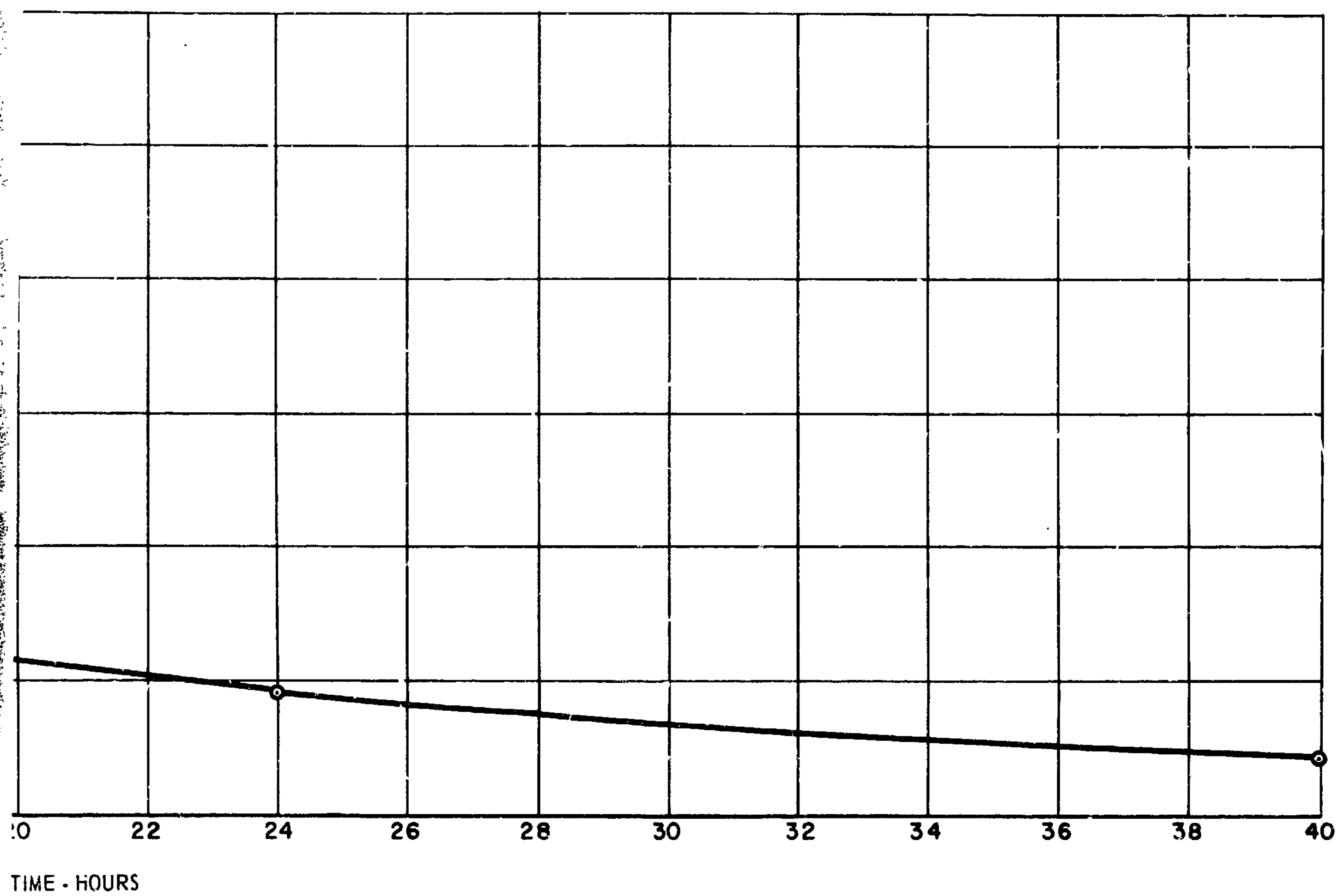


Figure 26. Liquid Hydrazine in CO_2 Detection Badge Exposed to 5 PSIA Oxygen

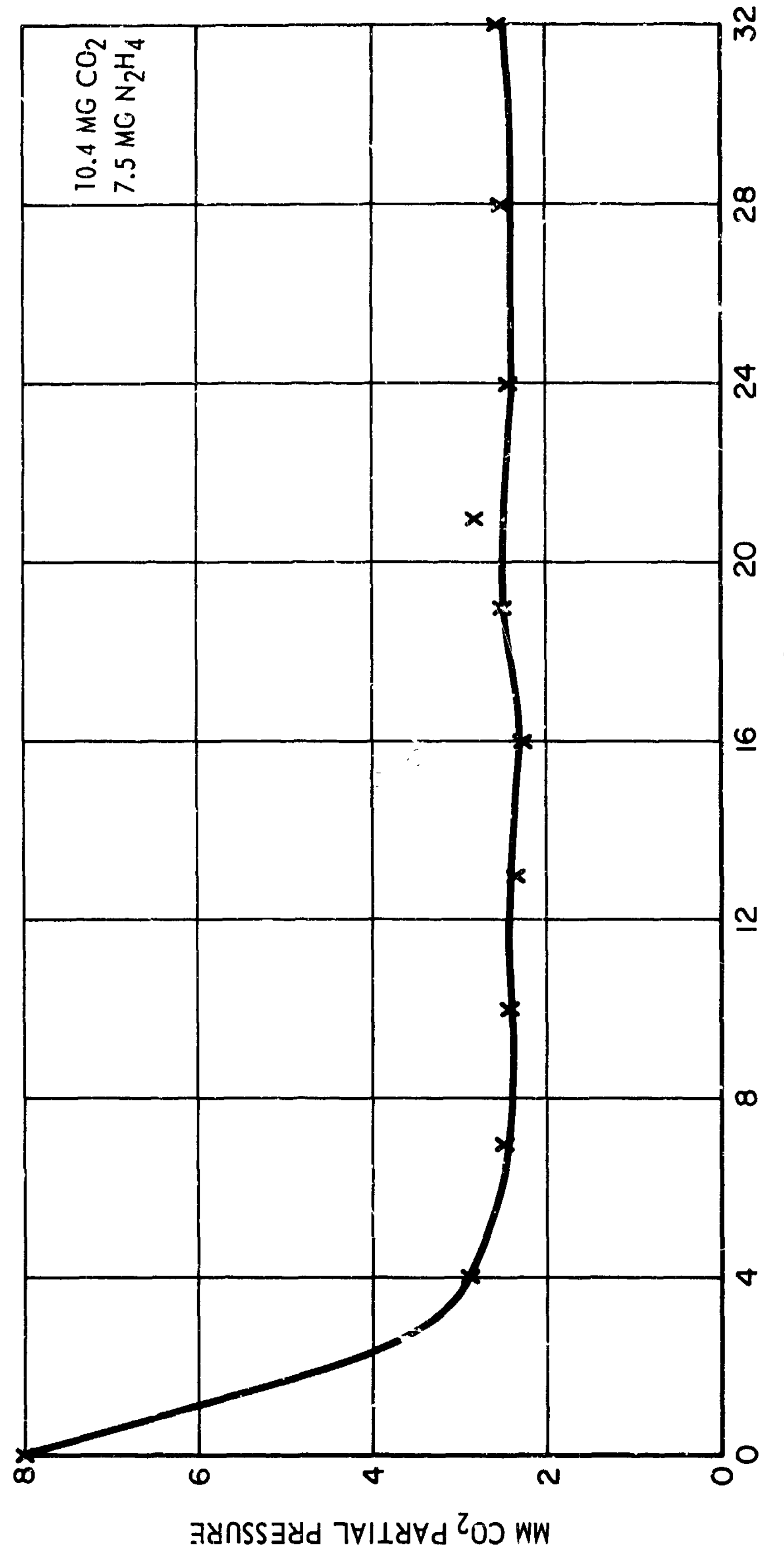


Figure 27. CO_2 Loss in the Presence of N_2H_4 in 5 PSIA Oxygen

rates would be less than this figure since smaller amounts of hydrazine would be more strongly absorbed by the filter paper and less hydrazine would be evaporated into the atmosphere.

This loss of hydrazine from the chemical tapes themselves is attributable to the direct reaction of oxygen with them. Reaction products are nitrogen and water.

7.4 Reaction of Hydrazine with Carbon Dioxide

Since the basis of response of the chemical detection tape is the reaction of the liquid hydrazine on the tape with carbon dioxide from the atmosphere, it was of interest to determine if carbon dioxide in the oxygen atmosphere would react with hydrazine vapor. The findings here could be quite significant, particularly since the tapes would probably only be opened when high concentrations of carbon dioxide were anticipated.

In this particular experiment a carbon dioxide-oxygen mixture was made in the 500-cc flask and the pressure reduced to 5 psia. The carbon dioxide partial pressure was 8 mm. After the total pressure in the vessel had been reduced to 5 psia, liquid hydrazine was injected into the flask with a hypodermic needle. The hydrazine was immediately vaporized with injection. The amount of hydrazine injected was sufficient to give an initial equimolar mixture of hydrazine and carbon dioxide. The total amount of hydrazine present within the container was 7.5 milligrams, and the total quantity of carbon dioxide was 10.4 milligrams at 5 psia.

After the admission of hydrazine into the container, the carbon dioxide partial pressure within it was determined as a function of time. The CO_2 analysis was carried out by gas chromatography.

Figure 27 shows the partial pressure of carbon dioxide as a function of the time of exposure to hydrazine in a 5-psia oxygen atmosphere. This plot shows that there is practically an instantaneous decrease in the CO_2 concentration with the introduction of hydrazine. The partial pressure of CO_2 decreases from 8 mm under the test conditions to approximately 3 mm within some 4 minutes. Beyond 4 minutes the CO_2 partial pressure levels off at approximately 2.4 mm. Thus, in just a few minutes the carbon dioxide level has decreased by about 5.5 mm from a level of 8 mm, as a result of its reaction with hydrazine. This corresponds to a carbon dioxide loss of 7.2 milligrams or 1.6×10^{-4} mole of carbon dioxide. There is no reduction in the CO_2 partial pressure unless hydrazine is present.

The initial amount of hydrazine present was 2.3×10^{-4} mole. Thus, it appears that nearly a 1:1 molar reaction between the carbon dioxide and hydrazine has occurred within just a few minutes. It is recognized that some hydrazine may have been rendered inactive as far as its reaction with CO_2 is concerned by adsorption on the side of the container.

A number of points are to be made in connection with the data summarizedin figure 27. First, when carbon dioxide and hydrazine are present in the atmosphere in equimolar amounts, practically all hydrazine is evidently removed. Second, under actual flight conditions there is a high probability that the carbon dioxide would be at a far higher concentration level than the hydrazine level in the atmosphere at any one time. Previous data show that one has to contend with a fraction of a part per million at most from any one badge. Under these conditions, in which excess carbon dioxide is present, the concentration of hydrazine should be brought to nearly zero.

These statements apply only to hydrazine removal by carbon dioxide. The effects of oxygen (and the catalytic effects to be discussed subsequently) should ensure that practically no hydrazine is present in the atmosphere. In addition, the amount of hydrazine or liquid hydrazine in the tapes should be reduced to almost zero by the interaction of oxygen and carbon dioxide.

7.5 Degradation of Hydrazine Vapor in 5 PSIA Oxygen

Since previous data had shown that hydrazine was oxidized by oxygen, it was of interest to determine the rate of loss of hydrazine vapor in a 5-psia oxygen atmosphere.

Approximately 100 micrograms of hydrazine were injected through a rubber septum into a 500-cc flask containing oxygen at 5 psia. The vaporized hydrazine injected in this way was left for a prescribed period of time. At the end of the prescribed time the container was analyzed for residual hydrazine by the methods described in paragraph 7.1. Different hydrazine injections were used in determining the effects of oxygen for different periods of time.

Accompanying this experiment as well as the other experiments involving the 500-cc glass flask, control measurements of hydrazine recovery were made. In carrying out control analyses, given amounts of hydrazine corresponding to approximately the maximum amount of hydrazine evolved from the tapes or purposely injected were used. Injections of hydrazine were made into a 5-psia atmosphere of N_2. The purpose of the control experiment was to ensure that the analytic technique was sound, and that all hydrazine present within the container, whether it be in the vapor form or adsorbed on the side of the container, was recovered. All of the control determinations made, in which known amounts of hydrazine were injected and recovered, checked quite well. Recovery was made by scrubbing the oxygen atmosphere of 5 psia through a 2N HCl water solution, followed by a washing of the container itself with a 2N HCl solution.

Figure 28 summarizes the data obtained in connection with the degradation of hydrazine vapor in an oxygen atmosphere of 5 psia. After some 10 hours of

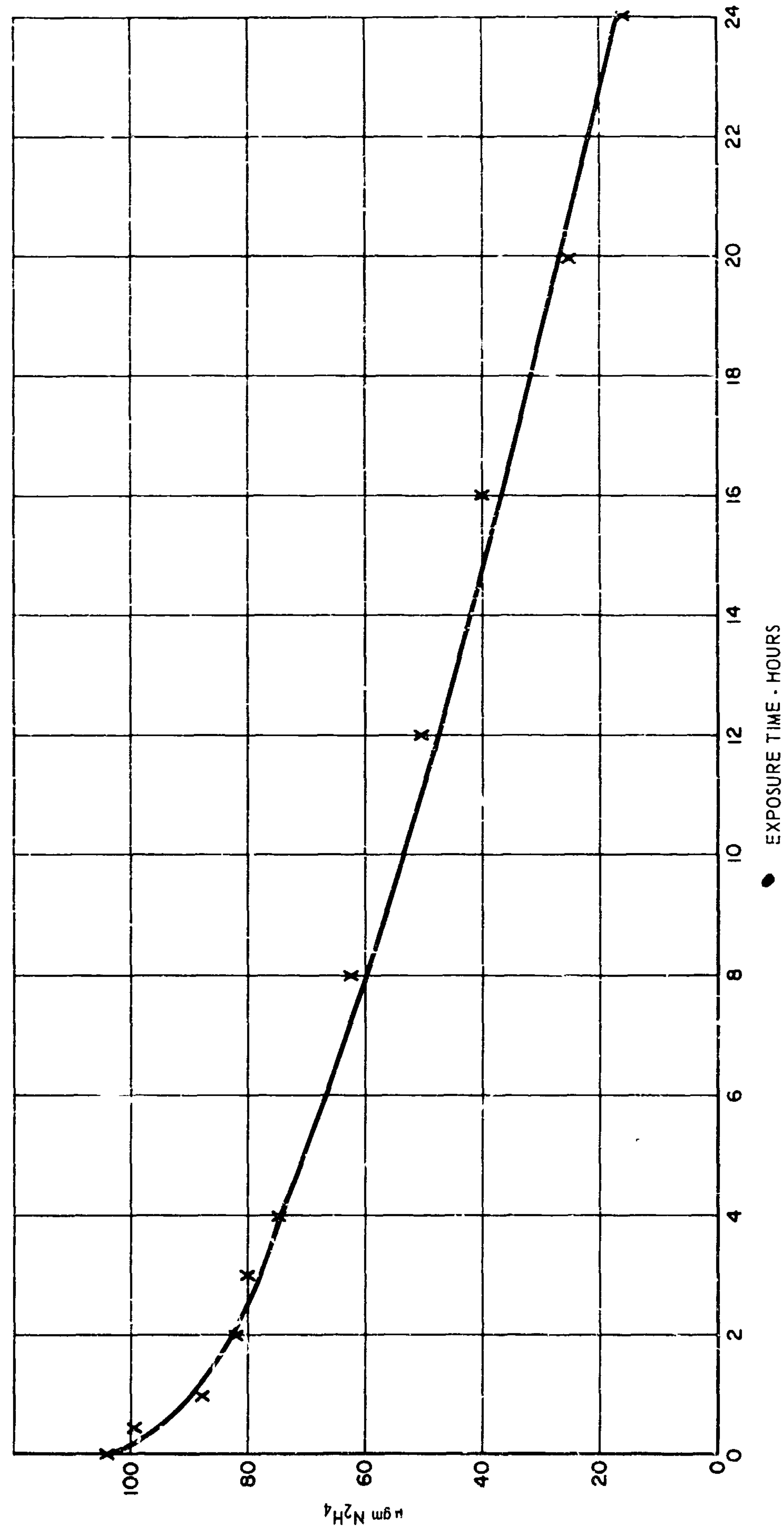


Figure 28. Disappearance of Hydrazine Vapor in the Presence of Oxygen (104 Micrograms of Hydrazine Exposed to 500-ml, 259-mmp Oxygen)

exposure to oxygen, the hydrazine concentration is reduced to approximately 50% of its initial value. After 24 hours it is down to approximately 17% of its initial value. These data would indicate that even for stored badges the hydrazine concentration would be materially reduced by oxidation; and this reduction coupled with that associated with the carbon dioxide reaction would lead to practically no hydrazine in the atmosphere. It is to be stressed that even without the oxygen and CO_2 effects, the hydrazine concentration realized from a single badge would only be in the fraction of a parts-per-million range. With the oxygen and carbon dioxide effects present, this concentration should be reduced to insignificant levels.

7.6 Catalytic Degradation of Hydrazine

The catalytic degradation of hydrazine by certain metallic materials is well known.* Copper and other metallic ions, for instance, readily promote its degradation. The experiments described here ably illustrate the catalytic effect of metallic surfaces on the degradation of hydrazine.

This experiment was undertaken in attempting to monitor by infrared the loss of carbon dioxide and hydrazine when they were present together in an oxygen atmosphere. In this experiment approximately 60 microliters of hydrazine were introduced into the 10-meter infrared gas cell, and the hydrazine was pressurized to 5 psia with oxygen. The infrared spectrum was then recorded on this mixture in the region of 2 to 15 microns, the rock salt region of the spectrum. Absorptions in the region of 13.5 microns were used in an attempt to monitor the hydrazine. In additional experiments carbon

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*L. F. Andrieth and B. A. Ogg, The Chemistry of Hydrazine.

dioxide was also added to the cell to give a partial pressure of 8 mm at 5 psia with the same amount of hydrazine still being present.

A close scrutiny of the recorded spectrum of hydrazine in oxygen, both with and without carbon dioxide being present, revealed that the concentration of hydrazine present was quite low. However, it was observed that the majority of the spectral peaks observed were characteristic of ammonia. As a consequence, it was concluded that almost all of the hydrazine had been catalytically converted to ammonia. This conclusion was substantiated by the fact that the spectrophotometric assay for the original hydrazine used showed the purity of the hydrazine to be approximately 96%. The hydrazine technique used in the assay was insensitive to ammonia.

It is to be noted that the conversion of hydrazine to ammonia was not dependent upon the presence of oxygen. Hydrazine was converted to ammonia in the 10-meter infrared cell when the hydrazine introduced into the cell was pressurized with nitrogen instead of with oxygen. The toxicity of ammonia formed is approximately 100 ppm. The ammonia is at least 20 times less toxic than the hydrazine from which it was formed.

The catalytic conversion of hydrazine to ammonia in the 10-meter infrared cell was believed to be associated with the cast iron sides of the cell. It is not impossible, however, that the aluminized front surface of the mirrors present promoted this conversion.

7.7 Discussion and Conclusions

The definition of toxicity of hydrazine as far as man is concerned leaves much to be desired. Toxicity data for the most part have been obtained on lower animal forms. The toxicity level for dogs is reported to be 5 ppm for an 8-hour period.[*] Due to the mass difference between man and dog, this toxicity level for man should be considerably higher.

It was recognized by experimentalists carrying out the hydrazine investigations that hydrazine was strongly adsorbed by the sides of the container in which the animal is placed. Because of this, it was necessary to continuously sweep the chamber with air containing the hydrazine at a set concentration level. The mixture of hydrazine in air in the toxicity studies was made just prior to the passage of the air-hydrazine stream into the test chamber.[*]

The results of these experiments show the same adsorption effects for hydrazine on the container walls, and the collected data indicate that in the static system at least 75% of the hydrazine present would be adsorbed.

These investigations definitely show that hydrazine vapor released from the carbon dioxide chemical detection badges is removed as a result of:

a. Adsorption on metallic surfaces.

b. Catalytic conversion on metallic surfaces to less objectionable products.

c. The slow reaction of hydrazine with oxygen.

d. The rapid reaction of hydrazine with carbon dioxide.

It is hard to envision in the light of all of these factors that any significant concentration of hydrazine could accumulate within the Gemini capsule. Even if the factors were not operative, the amount of hydrazine

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*K. H. Jacobson et al., "The Acute Toxicity of the Vapors of Some Methylated Hydrazine Derivations," AMA Arch. of Ind. Health (1955).

released from a single badge (figure 25) would lead to only approximately 0.3 ppm of hydrazine in the Gemini capsule atmosphere after 7 hours. Approximately 17 badges would have to be opened and stored for 7 hours for the total hydrazine concentration to approach 5 ppm if nothing happened to the hydrazine released. Certainly within this period of time the hydrazine concentration would be reduced to very small levels by the combined effects mentioned.

The minimization of the hydrazine vapor problem is further supported by the fact that oxygen of the air reacts with the liquid hydrazine remaining in the tapes.

The studies summarized in this section have covered logical factors that would lead to a reduction of hydrazine released from carbon dioxide chemical detection badges. There are likely to be others that have not been considered. For instance, no detailed evaluation has been made of the hydrazine removed or degraded by its passage through the lithium hydroxide-carbon dioxide scrubber. Bases are known to lead to a very pronounced degradation of hydrazine.*

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*C. C. Clark, Hydrazine.

8. TEST FOR TAPE RESPONSE IN 4000-FOOT/MINUTE FLOW AT A 5.5-PSIA PRESSURE

The response times of tapes were tested in a 4000-foot/minute flow, which corresponds approximately to a flow of 21 cubic feet per minute in a 1-inch-diameter hose.

First, some detectors were tested in this high flow of air at atmospheric pressure (14.7 psia). The results are shown in table 28.

TABLE 28

RESPONSE TIMES OF TAPES IN 4000-FOOT/MINUTE FLOW AT ATMOSPHERIC PRESSURE

Detector No.	Pressure (psia)	CO_2 Concentration (mm p.p.)	Response Time of Tape (Sec) 2 mm	4 mm
5X7	14.7	4	18	31
5Y12	14.7	4	15	31
5Y21	14.7	4	15	29
5Z31	14.7	4	16	36

These data show that the response time is on the low side, but still within the limits of the allowed error of 35 seconds, ±6 seconds.

The next 20 detectors, which were all quality-controlled badges ready for delivery, were tested in the same flow but at a 5.5-psia pressure. Each badge was tested at two different CO_2 concentrations. The glove box and badge opener constructed for the environmental evaluation of tape responses were used to perform these tests. The obtained values are given in table 29.

TABLE 29

RESPONSE TIMES OF DETECTORS IN 4000-FOOT/MINUTE FLOW AT 5.5-PSIA PRESSURE

Detector No.	Low CO_2 Conc. Side of Detector			High CO_2 Conc. Side of Detector		
	mm p.p. CO_2 Used	Response Time of Tape		mm p.p. CO_2 Used	Response Time of Tape	
		2 mm	4 mm		6 mm	8 mm
5V16	2	20	36	-	-	-
5V17	4	10	23	8	13	27
5V19	4	9	22	8	14	24
5V24	4	10	19	8	10	19*
5V25	4	10	20	8	7	16*
5V29	2	20	37	6	31	69
5W12	4	7	19	6	25	180
5W14	2	23	43	8	9	22
5W25	4	13	25	6	42	73
5X6	2	19	32	8	15	24
5X12	2	25	46	8	18	33
5X15	4	10	25	6	25	180
5X18	2	17	29	6	20	50
5X29	-	-	-	6	24	42
5X30	-	-	-	6	22	33
5X25	4	12	22	6	33	69
5Z4	2	19	31	8	8	28
5Z6	2	17	33	8	9	25
5Z9	4	8	23	8	11	34
5Z20	-	-	-	6	27	48
5Z24	2	22	43	8	11	33
5Z29	4	6	21	8	14	29
5AA8	2	15	32	6	20	47

*Too high CO_2 partial pressure.

To obtain a better table for comparison of the response times, the response times for the same concentrations of CO_2 on the corresponding tapes were collected. The results are given in table 30. From this table, it is evident that the response times of the tapes were faster than in the 2000-foot/minute flow. The accelerations of the two types of tapes, the Crystal Violet for 2- and 4-mm tapes and the Basic Fuchsin for the 6- and 8-mm tapes, were different. The Crystal Violet tapes accelerated more than the Basic Fuchsin tapes.

The environmental response of tapes at the 2000-foot/minute flow did not show an appreciable difference in tape response at reduced pressure. To make sure that these findings were correct, two badges were tested at 5.5 psia in a flow of 2000 feet/minute. The results are given in table 31.

TABLE 30

COMPILATION OF RESULTS SHOWN IN TABLE 29

2 mm Partial Pressure CO_2 2 mm Tape (Seconds)	4 mm Partial Pressure CO_2 4 mm Tape (Seconds)	6 mm Partial Pressure CO_2 6 mm Tape (Seconds)	8 mm Partial Pressure CO_2 8 mm Tape Seconds)
20	23	31	27
20	22	25	24
23	19	42	19*
19	20	25	16*
25	19	20	22
17	25	24	24
19	25	22	33
17	22	33	28
22	23	27	25
15	21	20	34
			33
			29
Average			
20	22	28	28

*The level of CO_2 partial pressure was too high.

TABLE 31

RESPONSE TIMES OF DETECTORS IN 2000-FOOT/MINUTE FLOW AT 5.5-PSIA PRESSURE

Detector No.	Low CO_2 Conc. Side of Detector			High CO_2 Conc. Side of Detector		
	mm Partial Pressure CO_2 Used	Response Time of Tape (Seconds)		mm Partial Pressure CO_2 Used	Response Time of Tape (Seconds)	
		2 mm	4 mm		6 mm	8 mm
5V18	2	32	58	6	29	62
5V23	2	36	65	6	39	69

The results obtained are normal and no acceleration is detected in the 2000-foot/minute flow and 5.5-psia pressure.

9. SUMMARY OF DELIVERIES OF CARBON DIOXIDE DETECTORS

To date, 1236 CO_2 detectors have been delivered to NASA Manned Spacecraft Center, Houston, Texas, commencing with the shipment on 28 May 1964 and ending with the one of 11 November 1965. Of the 1236 detectors, 123 were returned to Malpar because of failures in the badges after they had reached Houston.

Table 32 gives a breakdown of the delivery dates and the number of detectors shipped on these dates.

One hundred and twenty-three of the 141 detectors delivered on 4 and 10 May 1965 were returned to Melpar due to the high failure rate of the 18 badges that were opened at the Manned Spacecraft Center.

TABLE 32

DELIVERIES OF CO_2 DETECTORS

Delivery Date	No. of Detectors	Flight Qualified	Comments
28 May 1964	50	No	
26 June 1964	25	No	Extras
17 July 1964	50	No	
7 Aug. 1964	50	No	Extras
4 Sept. 1964	300	No	
20 Jan. 1965	300	No	
5 Mar. 1965	42	Yes	Used on GT-III. Should have been 50 detectors, but 8 were authorized for use in an additional acceptance test.
31 Mar. 1965	50	Yes	
4 May 1965	91	Yes	73 returned to Melpar
10 May 1965	50	Yes	Returned to Melpar
28 May 1965	28	Yes	Used on GT-IV
28 July 1965	52	Yes	Used on GT-V
4 Oct. 1965	48	Yes	Used on GT-VI
11 Nov. 1965	100	Yes	Used on GT-VII

10. SUMMARY OF WORK PERFORMED ON CO_2 DETECTORS

The purpose of this task was to develop and fabricate chemical tapes for the detection of carbon dioxide. These tapes were to have responded to a given partial pressure of CO_2 after having been stored under various conditions of temperature, pressure, and humidity.

The first problem encountered in the development of the tapes for the detection of CO_2 was to find the combination of reagents that would detect CO_2 at the specified concentration of 2, 4, 6, and 8 mm of partial pressure. The most specific color reaction for the detection of CO_2 that could be applied to this particular task was the decolorization of a triphenylmethane dye with a reducing base. This reagent system will change from colorless to a color when exposed to carbon dioxide. The color change is proportional to the concentration of CO_2.

After testing several dyes and reducing bases, the best results were obtained with hydrazine as the reducing base and Crystal Violet dye for the 2- and 4-mm tapes and Basic Fuchsin as the dye for the 6- and 8-mm tapes. Alcohols were known to be the best solvents for the triphenylmethane dyes and the hydrazine. After trying several alcohols, ethylene glycol was selected as the best solvent. Because of its high boiling point and viscosity, the ethylene glycol would not evaporate from the tapes as rapidly as would the lower boiling alcohols, such as ethanol and methanol. Many different concentrations of hydrazine and dye solution were tested before the most suitable mixtures were found for each of the four levels of CO_2 to be detected.

Whatman's No. 541 filter paper was chosen as the support for the reagent solution. It was chosen because of its high absorbency and medium hardness. Several other Whatman papers were tested, but all proved unsuccessful.

Reference colors for the sensitized tapes were prepared by dipping strips of the Whatman No. 541 filter paper in a specific concentration of the dye solution. A blue-violet reference was made with the Crystal Violet dye for use with the 2- and 4-mm tapes. The Basic Fuchsin was used to prepare a dark pink reference for the 6- and 8-mm tapes. Ethylene glycol was used as the solvent for each of the dyes. Several different concentrations of dye solution were tested before the correct intensity of color was obtained for each reference.

For the packaging of the tapes, a material had to be used that would resist the penetration of oxygen, CO_2, water, light, and to some extent heat from the air to the tapes. Several heat sealable plastics were tested for use as packaging materials. Aluminized Mylar-polyethylene laminate lined with 4-mil polyethylene was found to be the best material for the preparation of the badges for the CO_2 detectors.

Rather extensive tests were made to determine the best methods of preparation for both the reference tapes and the sensitized detecting tapes. Tests were run on the length of soaking time to be used, the number of blottings to be made and length of time of each blotting, the length of time the tapes could be exposed to nitrogen atmosphere in the dry box, and the temperature and humidity at which the dry box should be kept.

Reliability studies were made to determine the reader's error, the reproducibility of the tapes, and the effect of environmental conditions on the tapes.

Storage and environmental tests were conducted on the detectors. The detectors were stored under different conditions of temperature and humidity. Tapes were also tested in various conditions of temperature, pressure, and humidity to determine the effects of environmental changes on the response times of the tapes.

Because of the toxicity of hydrazine, several tests were conducted to determine the degree of evolution of hydrazine from the CO_2 detection tapes. The amount of hydrazine evolved from the detectors in a given time was below the toxicity limit for man.

The response times of the CO_2 tapes were taken in a 2000-foot/minute linear flow of air and a specific partial pressure of CO_2, as was required in the contract. Because of the findings later in the program that the flow from the suits of the astronauts was 4000 feet/minute, some tapes were also tested at the 4000-foot/minute linear flow to give a comparison of the response times at the two different flow rates.

As a final product of the research and development effort described above, a CO_2 detector was manufactured. This detector was able to perform with very high reliability and to pass the requirement of flight qualification. The flight qualification test plan is described in document CSD-G-137 (dated 2/23/65), prepared by NASA Manned Spacecraft Center, Crew System Division. For each Gemini flight the required number of such badges were delivered and each lot passed the acceptance test before delivery.

11. SUGGESTIONS FOR POSSIBLE IMPROVEMENT OF CO_2 DETECTORS

11.1 Tetraethylenepentamine Replacement of Hydrazine

The difficulties encountered in realizing full stability of the chemical tapes at elevated temperatures have caused Melpar to continue its efforts to improve the tapes insofar as possible. For this reason, tetraethylenepentamine (TEPA) was experimentally substituted for hydrazine as the basic reducing agent. TEPA was selected primarily because of its high boiling point (333°C), and it was hoped that with this reagent an environmental temperature of 160°F could be maintained for 48-hour periods.

Two concentrations of solutions using TEPA and Crystal Violet were prepared and likewise of the TEPA-Basic Fuchsin. A 24% TEPA and 32% TEPA solution of Crystal Violet (0.1%) tapes was prepared. Basic Fuchsin (0.2%) tapes of 20% TEPA and 32% TEPA wer made. The tapes were dipped and blotted in the same manner as previous tapes. From 24 tapes of one concentration, 8 were packaged in an aluminized Mylar package and set aside. Four bags of tapes (six tapes to a bag) were placed in the oven at 120°F for periods of 16, 32, 48, and 64 hours. Each of the four concentrations of tapes was handled in this manner.

After this period of heating, both the unheated and heated tapes were tested for response times to carbon dioxide. The Crystal Violet tapes were tested at 2- and 4-mm partial pressures of CO_2 and the Basic Fuchsin tapes were exposed to 6- and 8-mm partial pressures of CO_2. The tapes that had been in the oven at 120°F for 48 hours were than placed in a 160°F oven for 18 hours. The response times of these tapes were again recorded.

Table 33 shows the results of the response time tests on the TEPA tapes. As can be seen from the response times, this test was run to determine the effect of heat upon the tapes and no great effort was made to obtain a 35-second response time. In future work, tapes should be prepared with concentrations of TEPA that will give approximately 35-second responses to carbon dioxide. Each response time listed in table 33 is the average of three readings.

As can be seen from the results, the Crystal Violet-TEPA tapes when heated for 16 hours at 120°F slowed down from their original (unheated) response times, but they did not seem to change greatly when they were heated for longer periods of time at this same temperature. When the Crystal Violet-TEPA tapes were heated for 18 hours at 160°F, their response times continued to increase. From this information, it seems that the response times of the Crystal Violet tapes should be brought to equilibrium by heating the tapes for possibly 48 hours -- 64 hours at 160°F instead of the 120°F used in this series of tests.

The Basic Fuchsin-TEPA tapes like the Crystal Violet gained in response time within the first 16 hours of heating at 120°F. But when heated for 18 hours at 160°F, the Basic Fuchsin tapes showed only a very slight increase in response time. It appears that either 120° or 160°F could be used as an equilibrating temperature for the Basic Fuchsin-TEPA tapes.

From the very meager results obtained on the TEPA tapes thus far, it seems very likely that these tapes will withstand a temperature of 160°F for about 48 hours.

TABLE 33

RESPONSE TIMES IN SECONDS OF TETRAETHYLENEPENTAMINE TAPES

	Crystal Violet Tapes				Basic Fuchsin Tapes			
	24% TEPA Exposed to:		32% TEPA Exposed to:		20% TEPA Exposed to:		32% TEPA Exposed to:	
	2 mm CO_2	4 mm CO_2	2 mm CO_2	4 mm CO_2	6 mm CO_2	8 mm CO_2	6 mm CO_2	8 mm CO_2
Unheated	22	15	51	29	9	7	20	15
16 hrs at 120°F	31	19	75	47	13	11	31	22
32 hrs at 120°F	33	19	69	32	13	9	31	20
48 hrs at 120°F	41	20	62	40	12	10	32	22
64 hrs at 120°F	33	19	52	34	13	10	27	18
48 hrs at 120°F and 18 hrs at 160°F	--	38	--	63	--	12	--	24

11.2 Improved Packaging Materials

Melpar's experiences in manufacturing the completed badge detectors have pointed up the fact that the materials used in the packaging, while for the most part satisfactory, have some weaknesses which could be eliminated from the final package, yielding a superior product and one which could be easier to make. A primary problem has been the permeability of the Mylar film to oxygen. The entry of oxygen into the completed detector lessens the stability and thereby the shelflife of the completed detector. Table 34 gives the permeability differential of several products to gases.

TABLE 34

PERMEABILITY OF O_2 and CO_2 THROUGH DIFFERENT PACKAGING MATERIALS

Gas	Mylar	Capran	Tedlar	Aclar	Polyethylene
O_2	6	2	3.2	7	920 (30°C)
CO_2	16	5.9	11.0	16	4200 (30°C)

It may be seen from the table that a material such as Tedlar is less permeable to the gases of interest than are Mylar or Aclar, and that all of these are far better than polyethylene. However, Tedlar does not lend itself well to seals, whereas Aclar is very suitable for sealing to itself and for lamination with other materials such as aluminum foil. One possibility that should be explored relative to improving the package is an Aclar-aluminum foil-Aclar laminate, which should prove to be far less permeable than the present materials. Other laminates should be examined which combine the useful properties of several materials. The result will be a package with an extended storage life and superior manufacturing properties. This will permit more economical manufacturing methods because fewer waste packages would be made.